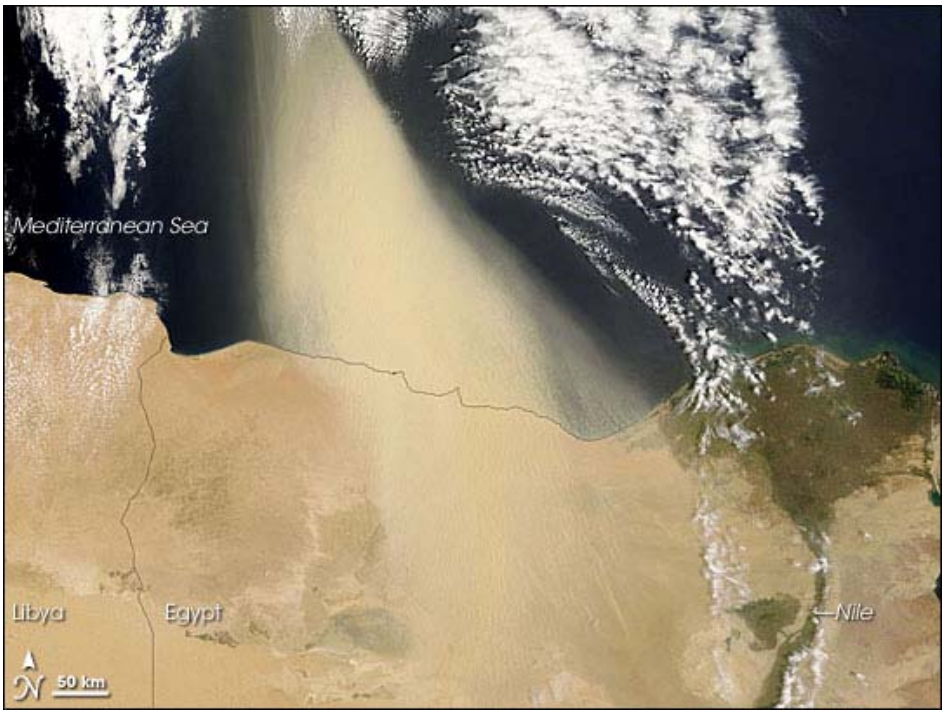
Contribution of natural sources to air pollution levels in the EU - a technical basis for the development of guidance for the Member States

Luisa Marelli



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SUMMARY

Exceedences of air quality limit values represent breaches of Community law which can have significant legal consequences for the Member States. For some existing limit values, such as those in directive 1999/30/EC (1st Daughter Directive), an exceedence which is caused by particular natural sources can be ignored for the purposes of ensuring compliance with Community law. For example, Article 2.15 of the first daughter directive defines "natural events" as volcanic eruptions, seismic activities, geothermal activities, wild-land fires, high wind events or the atmospheric resuspension or transport of natural particles from dry regions.

A new air quality directive proposal is currently being negotiated in the Council and the European Parliament and this is likely to extend this principle to natural (non-anthropogenic) sources of pollution generally so long as the "natural contribution" can be quantified and documented. This could include sea-spray and biogenic organic aerosol amongst other materials. The aim of this report is to document that information and methodologies which are available to permit Member States to determine and document natural sources of air pollution. This information will later be incorporated into specific guidance to be developed by the European Commission in the context of implementing the new legislation once adopted by the Council and the European Parliament.

In this report different types of natural sources contributing to PM levels in Europe are identified according to experts' judgment and based on literature studies. The methods currently implemented by research groups of the Member States for the identification and quantification of natural sources are also described.

The content of this report is based on discussions with experts from various Member States, on the results of a questionnaire which has been circulated to experts of all EU Member States, on available literature studies and on the outcomes of a workshop on "Contribution of natural sources to PM levels in Europe" organized by the JRC in Ispra in October 2006; the workshop aimed at identifying the natural sources that may contribute to the different PM levels in Europe and the available methods to quantify this contribution.

In relation to the issue of compliance with Air Quality limit values the most important PM contributions by natural sources in Europe may be identified as wind-blown, long-range transported mineral dust and sea salt. However, a multitude of natural sources may affect PM levels at lower, but still appreciable extents:

- Primary biological aerosol particles (PBAPs), which include individual units as pollens or spores, as well as fragmented material as plant debris.

- Biogenic non-sea-salt sulfur aerosol

-Volcanic activities, limited to restricted areas in Europe and only occasionally causing exceedences of PM limit values.

PM of other natural sources that originate outside of the EU that are transported over long distances into Europe should also be considered. Androgenic pollution events outside the EU which contribute to elevated air pollution levels in the Member States could also justify such an exceedence for the purposes of compliance with EC law, however, this is a distinct issue outside the remit of this report and which would need to be notified to the Commission on an ad-hoc basis.

As extensively discussed at the workshop, other sources may be natural in origin but strongly influenced by human actions. Among these are:

- Secondary organic aerosol (SOA) formed by oxidation of biogenic volatile organic compounds (VOC) in particular during summer time in vegetated areas. The most important interaction of biogenic VOC is with compounds that may be both anthropogenic and natural (NO_x and O_3), the associated complex chemical pathways still being an area of active research.

- Biomass burning and forest fires, generally of anthropogenic origin, may be in many cases controlled with appropriate actions

- Re-suspended particles may be of natural origin (crustal dust) and re-suspended by human activities, or anthropogenic.

For the purposes of compliance with air quality limit values, experts agreed that only contributions to PM from natural sources and that may not be influenced by human action can be deducted from PM levels according to the indications given in the directives. All contributions derived from interactions between natural and anthropogenic actions should no be considered.

A number of methods for analyzing natural contributions to total PM are implemented by Member States; the apportionment may be done using different methodologies: 1) using routine measurement methods available in the existing Air Quality monitoring networks, 2) using information obtained in parallel from background stations and 3) using advanced tools implemented by research groups, including experimental analysis, satellite imaging and modeling. Many of these procedures however have the disadvantage to require continuous sampling and analysis for a number of components and may be very expensive because of the advanced instrumentation that they require; consequently they cannot be applied routinely in EU air quality monitoring networks.

A simple method for the identification of natural contributions to PM consists of the combined monitoring of PM_1 and PM_{10} concentrations. This methodology is based on the observation that

mineral dust and sea salt, the most important natural source contributions to PM, are mainly in the coarse fraction (>90%). However, a change in the legal metrics of PM from the actual PM_{10} and $PM_{2.5}$ to a future PM_1 appears not feasible in the near future.

Some procedures are implemented by few Member State on routine basis. Meteorology, satellite imagery and modeling tools are widely used to detect natural PM episodes. For those days exceeding the limit values, levels of natural PM contributions measured at the regional background monitoring sites are subtracted from the levels measured at urban agglomerations in order to determine the natural or anthropogenic origin of exceedences. This procedure is applied by a few Member States for African dust outbreaks.

1. INTRODUCTION

1.1 Background

Atmospheric pollution due to airborne particulate matter is of great impact in numerous EU Member States and Eastern Countries, where the limit values imposed by the European Union Directive 1999/30/EC are often difficult to be attained. Air pollution levels depend to a considerable extent on anthropogenic emissions; however, in some areas large amounts of PM can be emitted from various sources of natural origin or transported from regions outside the EU.

It has been estimated that the natural contribution to PM may range from 5% to 50% in different European Countries; background annual average PM_{10} mass concentration for continental Europe is 7.0 ± 4.1 μg/m^3 (Putaud et al., 2004), and is due to natural sources as well as to anthropogenic long range transported particles. This natural background level shows regional variations, and in many cases (in particular for the Southern Mediterranean Countries) naturally emitted PM may cause exceedences in air quality standards.

Exceedences of air quality limit values represent breaches of Community law which can have significant legal consequences for the Member States. For some existing limit values, such as those in directive 1999/30/EC (1st Daughter Directive), an exceedence which is caused by particular natural sources can be ignored for the purposes of ensuring compliance with Community law. For example, Article 2.15 of the first daughter directive defines "natural events" as volcanic eruptions, seismic activities, geothermal activities, wild-land fires, high wind events or the atmospheric resuspension or transport of natural particles from dry regions.

A new air quality directive proposal is currently being negotiated in the Council and the European Parliament and this is likely to extend this principle to natural (non-anthropogenic) sources of pollution generally so long as the "natural contribution" can be quantified and documented. This could include sea-spray and biogenic organic aerosol amongst other materials. The aim of this report is to document that information and methodologies which are available to permit Member States to determine and document natural sources of air pollution. This information will later be incorporated into specific guidance to be developed by the European Commission in the context of implementing the new legislation once adopted by the Council and the European Parliament.

However, the estimation of natural sources is quite difficult by routine measurements performed in monitoring networks, and only few Member States routinely implement methods for the identification and quantification of natural processes on PM levels .`

On request of the European Commission's DG Environment the Joint Research Centre contributed to clarify the notion of natural sources in the Community legislation and to provide guidance to the Member States on what may be considered as being "natural" and rural background, and which common methods facilitate the assessment of natural contributions or natural events.

1.2 Objectives

This study aims at the implementation of the following issues:

1) Clarify the notion of natural sources in the current legislation and reach consensus on the definition of "natural sources of PM".
2) Collect information on methods to attribute the fraction of PM that is of natural origin, including source apportionment and modeling, and analyze available information from monitoring and modeling.
3) Draft guidance on methods for the assessment of natural sources contribution to PM after consultation with experts

In order to implement objectives 1) and 2) and in particular for the definition of "natural sources", a detailed questionnaire was sent to experts from the Member States; the discussion involved national experts in the field of source apportionment of particles, as well as NatAir and AQUILA networks and CAFÉ Steering Group members. The questionnaire focused on the following questions:

1. What should be considered as "natural events" contributing to PM pollution?
2. Comparing to the definition in the present Legislation, which other sources of natural PM should be added?
3. Which typical natural PM sources do occur in Member State and which is the impact on PM levels?
4. Which qualitative or quantitative methods are presently implemented to evaluate the contribution of Natural Sources to PM levels?
5. Presence of zones or agglomerations where the air quality standards for PM are exceeded owing to natural sources?

6. Current praxis to subtract natural contributions to PM levels when reporting exceedences of PM limit values?
7. Are spatial information in form of maps accounting for natural PM concentrations available?

Following this preliminary consultation, a workshop on "Contribution of natural sources to PM levels in Europe" was organized by the JRC in Ispra in October 2006; the workshop aimed at defining and identifying the origin of the natural sources that may contribute to the different PM levels in Europe and the available methods to quantify this contribution. The contents of this report, based on the discussions with experts, represent the experiences of Member States in the identification and evaluation of the natural contribution to PM and describe the methods implemented by routing networks, national laboratories and research groups in Europe.

2. Review of the definition of Natural Sources of PM

Wind blown, long-range, transported mineral dust and sea salt are the most important natural sources contributing to aerosol loading in Europe. They mainly affect air quality standards in Mediterranean area countries, as they are close to arid and semi-arid regions in North Africa (e.g., Sahara and Sahel deserts). IPCC (2001) estimated emissions for the year 2000 of 1800 Tg/yr for soil dust and 1500 Tg/yr for sea salt in the Northern hemisphere, with more than 95% in the coarse (>1 μm) fraction of PM. In addition to these two PM components, as extensively discussed with experts from the Member States, a multitude of natural sources may affect PM levels at lower, but still appreciable extents.

According to the definition of Directive 1999/30/EC the following sources of PM must be considered as natural in origin: volcanic eruptions, seismic activities, geothermal activities, wild-land fires, high-wind events, atmospheric re-suspension or transport of natural particles from dry regions. However it is common opinion of experts and Member States representatives that a review of this definition, in particular in view of the possibility of subtracting the natural contribution, is necessary; different aerosol sources not specifically mentioned in the legislation could additionally be considered as natural sources and should be included in the definition, whereas sources of particles formed by the interaction of natural with anthropogenic compounds as well as all natural emissions that can be controlled to some extent by appropriate human-initiated measures should not be subtracted from total PM levels.

In addition to emissions from volcanic, seismic or geothermal activities, and dust intrusion from outside Europe (e.g. Sahara or Sahel desert) the following sources have been identified by

experts from Member States as to be considered “Natural” and subject to subtraction from PM values:

- Sea-salt (as already proposed in the new CAFÉ Directive under art. 2); it may contribute to PM_{10} mass concentration not only in the Mediterranean basin, but also in some coastal areas of Northern countries. Hence, sea spray formation occurs during high wind episodes, in particular in Northern EU: hence, these events occur during relatively low ambient PM_{10} concentration. In practice, days of high PM_{10} levels may be only partially affected by significant sea-salt formation so that sea salt influences annual average more that daily average PM_{10}.
- Primary biological aerosol particles (PBAPs); they include individual units as pollens or spores, as well as fragmented material as plant debris. Their contribution to PM_{10} is very limited in winter time, and may account for 5% of PM_{10} in periods when vegetation is particularly active.
- Biomass burning and forest fires; since they are generally of anthropogenic origin, and in many cases may be controlled with appropriate actions, Member States should therefore communicate this contribution in view of the possibility of deduction only if the emissions are transported from regions outside the EU.
- Other sources that originate outside the EU, not necessarily of natural origin, and that are transported into Europe should also be considered. Since countries affected by these emissions (mainly Northern and Eastern areas) can hardly take any action against them it was argued that their contribution could be deducted from PM values. However, a clear identification and quantification of such events is difficult.

On the contrary the following sources are still problematic as they can not be considered as to be totally natural in origin:

- Secondary organic aerosol (SOA) formed by oxidation of biogenic volatile organic compounds (VOC) may be very important, in particular during summer time in vegetated areas. However, the most important interaction of biogenic VOC is with compounds that may be both anthropogenic and natural (NO_x and O_3), the associated complex chemical pathways still being an area of active research. Consequently, it has been agreed that at the moment it is not possible to identify clearly the portion of biogenic SOA that is completely natural and to eliminate its interactions with anthropogenic compounds. Thus, given current knowledge the possibility to subtract its contribution from measured PM_{10} cannot be suggested and a much more clear picture of the process and its implication on AQ should be gained.
- Re-suspended particles are also critical issue, since they may be natural in origin (crustal dust) and re-suspended by human activities, or originally anthropogenic but re-suspended by natural

actions (wind blown dust). As these two contributions may hardly be distinguished it was agreed by experts that re-suspension should not be accounted for in total PM deductions.

3. Assessment of natural sources contribution to PM in Europe

3.1 Long Term transport of desert dust

Resuspended and transported African desert dust particles have a strong impact on atmospheric visibility and aerosol composition as well as on PM levels in particular in Southern Europe; the contribution of transported Saharan dust may reach more than 60% of total PM_{10} in Mediterranean countries during a strong dust pollution event (Fig.1); on average, 26% of the central Mediterranean surface was covered by Saharan dust in the year 2001 (Barnaba and Gobbi, 2004). Also on a global scale the mineral fraction is the main component of aerosols (IPCC, 2001).

Dust emission is caused by the wind blowing above dry and scarcely vegetated soils, where particles with a diameter of ten to hundreds of μm are present (Mahowald et al., 2005). These particles are moved by the wind and bounce on the surface (saltation) causing the dislodgement of smaller particles (with a diameter <20 μm) that can be lifted into the atmosphere and travel long distances.

This long distance transport of mineral particles is related to the generation of massive resuspension processes in arid zones like North Africa. Natural episodes of high PM levels in Southern Europe are more frequent in spring/summer periods, when climatic conditions are favorable for the transport of dust from North Africa into eastern Mediterranean (spring) and into western Mediterranean regions (summer), as satellite observations, modeling and ground-base measurements have shown (Fig.1).

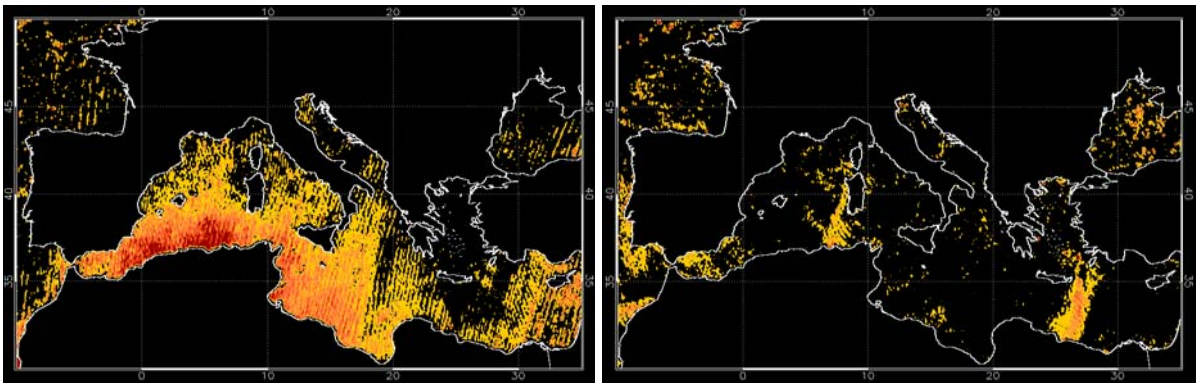


Fig.1: mean seasonal contribution of desert dust to aerosol optical thickness at 550 nm over the Mediterranean basin during summer (left side) and winter (right side) time (Barnaba and Gobbi, 2004. Presented at the workshop on "Contribution of natural sources to PM levels in Europe"JRC ISPRA, October 2006)

Grain size distribution of particles transported by these processes strongly depends upon the source area (the Sahara o Sahel deserts in North Africa) and upon the location of the receptor area with respect to the emission. Thus, during episodes of transport of particles towards the American continent the grain size mode is within the fine fraction (0.1-1.0 μm), while during the episodes over the Mediterranean in summer or the Canaries in winter the main size mode is in the coarse fraction (1-25 μm). According to experimental results in Europe, dust particles can account for a fraction of both PM_{10} and $PM_{2.5}$, whereas PM_1 is not influenced by this component. As a result of the questionnaire (question 3), Southern Europe Member States (mainly Spain, Italy, Portugal and Greece) are quite often affected by Saharan dust episodes (i.e. more than 20 episodes per year of PM_{10} exceeding limit values due to dust intrusion were identified in Spain), while their influence in Northern countries is practically negligible (1 to 2 episodes per year of exceedences of limit value identified in UK).

3.2 Marine aerosol

Marine aerosol represents a significant fraction of the global aerosol loading and is characterized by two different aerosol types: one of primary origin, mainly sea salt (although recent findings suggest also the presence of a primary organic source, linked to phytoplankton bloom, O'Dowd, 2004) produced by the wind breaking sea waves' crests, and one of secondary origin, mainly non-sea-salt sulphate (nss-sulphate) and organic matter, both produced by gas-to-particle conversion of biogenic compounds (in clean conditions, otherwise also anthropogenic emissions can be involved).

Typically, marine aerosol size distributions range from about 5 nm to 10 μm or more and four distinct modes can be identified: an ultrafine mode, with particles diameter approximately. ranging from 5 nm to 20 nm, an Aitken mode, from about 20 to 80 nm, an accumulation mode, from ca. 80 to ca. 300 nm and a coarse mode, at super-micrometer sizes. Usually, the Aitken mode and the accumulation mode are the strongest contributors to the number concentration of aerosol particles, while the coarse fraction particles dominate the surface area distribution.

Considering the size segregated chemical composition, sea salt is the major component of the super-micrometer fraction, although it may be present also in the sub-micrometer size range. Sea salt particles are produced at the ocean surface by the bursting of air bubbles resulting from entrainment of air induced by wind stress. Each bubble can generate jet drops with a typical size of 5 μm diameter, and film drops in the sub-micrometer range; the number and mass concentrations of sea salt particles are exponentially related to wind speed (O'Dowd et al, 1997). In the year 2000, according to IPCC estimates, the total sea salt flux from ocean to atmosphere was about 3400 Tg/y, while according to AERO and EMEP emission inventories, during the year 2000 in Europe sea salt emissions were estimated to be 87 Tg.

By contrast, the fine fraction of marine aerosol is enriched in nss-sulphate and organic matter. The pathway leading to the formation of nss-sulphate and methanesulphonic acid (MSA, an organic compound typical of the marine aerosol) as end products of the oxidation of DMS-derived SO_2 is well known, but the characterization of the organic compounds in the fine fraction of marine aerosol is still largely uncertain.

Among the various components of marine aerosol, sea salt is quantitatively the major contributor to marine aerosol mass (especially in the super-micrometer fraction) and it is therefore the one to be considered when evaluating the natural contribution of marine aerosol to PM loadings. Furthermore, the inorganic ions making up for sea salt are easier to chemically characterize (e.g. by means of ion chromatography), with respect to the organic fraction, and consist mainly of sodium, chloride and magnesium. Conversely, not only the chemical composition of the secondary components can not be fully resolved due to the presence of organic matter, but also it is not trivial to discriminate between secondary aerosols produced by biogenic emissions and those due to anthropogenic emissions.

3.3 Primary biological aerosol particles

Primary biological aerosol particles (PBAPs) comprise material that originally derives from biological processes (Jaenicke, 2005). This material has been transferred into the atmosphere

without change in its chemical composition. A distinction is needed between particles which maintain their physical characteristics, specifically their cellular structure, and material which is the result of a fractionation process. The difference is significant as for the former particles much more distinct properties can be identified, concerning particle size, mass, and chemical composition. Individual structural units that are present in the atmosphere include pollen, spores, bacteria and viruses. In contrast, fractionated material may occur over a much larger size range. Fractionated PBAPs can be identified by their composition. They may consist of plant debris as well as animal material. Like any atmospheric aerosol derived from a friction process, PBAPs will be more abundant in the “coarse” aerosol mode particles (larger than 1 µm diameter).

In the atmosphere, pollens are typically of a size of 30 µm and above, with a few exceptions (birch pollen) as small as 10 µm. Even these small pollens are not element of PM_{10} (Riediker et al., 2000). Allergenic material derived from pollen is known to also occur at smaller particle sizes, but only as a consequence of a fractionation process (see e.g. Rantio–Lehtimäki et al., 1994; Spieksma and Nikkels, 1999).

Fungal spores, bacteria and viruses are clearly differentiated by their mass. While the size of spores is in the range of 13 pg C (Bauer et al., 2002a; total mass: 33 pg, see Bauer et al., 2006b), bacteria are about three orders of magnitude smaller (17 fg C: see Bauer et al., 2002b; Sattler et al. 2001). Still far smaller mass has been attributed to viruses.

Lacey and Venette (1995) provide information on number concentrations of PBAPs. At a count of 1000 pollen grains m^{-3}, assuming 50 µm diameter and a density of 1, this results in 65 µg/m³. In extreme cases even 8000 m^{-3} have been observed. Even if pollen can be carried over large distances (Sofiev et al., 2006), they tend to deposit due to their large size, thus high concentrations will be limited close to their emission sources.

Again Lacey and Venette (1995) report number concentrations on spores. While moss and fern spores are present at a few thousand per cubic meter, the number of fungal spores can be as high as 10^5, under special circumstances up to 10^6 m^{-3}. With a spore mass of 33 pg (see above; this is consistent with a sphere of about 4 µm diameter), concentrations of 0.3 µg/m³ can be derived – or up to 3 µg/m³, when referring to the highest counts. Spores can be assumed to remain suspended in air for an extended period of time. Lacey and Venette (1995) refer to plant surfaces, but also to wind-blown soil as important sources of fungal spores in the atmosphere.

Numbers found for airborne bacteria are typically smaller than for spores. Due to their vastly smaller mass, their contribution to total aerosol mass becomes negligible. The same is the case

for viruses, which are not considered to occur as individual particles but instead to form clusters or droplets.

Assessment of bioaerosols is important for animal breeding. Indoor concentrations and emissions from animal houses have been quantified as a function of the breeding cycle and the distance from the potential release site. While clear differences can be observed for the number of colony forming entities (CFE) of bacteria downwind of animal houses, background concentrations of fungal spores do not permit an identification of a plume (Hartung et al., 2005). It may be concluded that fungal spores are ubiquitous.

Within the wide range of atmospheric primary particulate matter, biological particulate matter has not been investigated as deeply as the other particulate sources.

Few studies brought some information in terms of mass loading, but a significant fraction of the plant matter and debris/fragments found in fine particle OC may be related to fungi and pollens.

According to the results reported by Mathias-Maser (1995) and Jaenicke (2005), PBAP concentrations do not show a seasonal trend, but their composition varies through the year: in spring pollen is prevailing, while in winter decaying cellular matter is more abundant. Furthermore, the composition of PBAP is related to the wind direction with respect to the location of sources: rural regions provide a larger amount of pollen and spores (i.e. larger particles), whereas urban regions favor the formation of bacterial aerosol, i.e. smaller particles. Casareto et al. (1996) though, observed that bacteria are often attached to bigger mineral particles, therefore they are predominantly found in the coarse fraction as well.

Measurement of pollen allergens in fine PM samples based on protein content suggests that 15% of the weight was comprised of pollen fragments (Schappi et al., 1996). A paper published by Namork (Namork et al, 2006), based on allergenic reaction, does not provide any quantitative information on pollen contribution but the data can be useful to evaluate the presence of pollen in PM in some European cities. Results showed that the contribution of pollens is more related to humidity and air circulation than to plant flowering.

Preliminary results of the NATAIR Project (see chapter 5) indicate that the annual emission factor of PBAP is 24 Kg/Km^2, and that in Europe more than 200000 tons PBAPs are emitted per year. These results are based on atmospheric concentrations, rather than on source strength, since emitting processes are not yet defined and are still biased by high uncertainties.

At this point, little is known about the generation process of PBAPs. Without information on the generation process, it is also difficult to assign the responsibility of an emitter. While PBAPs are definitely the result of biological processes, it is not at all clear whether such processes should be considered natural. Plant debris may be triggered by agriculture, the release into the

atmosphere enhanced by wind blowing along harvested stubble fields, agricultural machinery of even road traffic. Fungal spores can be the result of composting agricultural waste, of specific soil treatment methods, or similar. At least some of the material included here has classically been reported under PM emissions from agriculture (e.g., animal housing).

From atmospheric concentrations alone, without a proper source term, it is almost impossible to correctly attribute the origin of PBAPs in the atmosphere. Consequently, an exemption from a requirement to reduce the concentrations, being a natural source, can not be substantiated. From the perspective of the citizen's health, there is no reason for a differentiation between this source being natural or anthropogenic: as stated above, no information is available that this source, if at all natural, is less hazardous – or to the contrary, atmospheric concentrations observed from natural sources should rather lead to enhanced abatement of man-made PM emissions in order to arrive at a balanced situation of acceptable air quality.

3.4 Biomass burning and forest fires

Forest fire emissions may affect PM levels in particular in summer time in forest areas (fires during summer 2005 in Portugal are an example); however some Member States suggest that, since wild-land fires are mainly anthropogenic in origin, they should not be considered as "natural sources of pollution" in the Directive.

3.5 Resuspended particles

There are considerable quantities of resuspension of wind blown dust on road and pavement surfaces which arise from ingress of soil on vehicle tires and from the atmosphere, from the erosion of the road surface itself and from degradation of parts of the vehicle, especially the tires. Since these particles lie on a surface which readily dries and is subject to atmospheric turbulence induced by passing vehicles, this provides a ready source of particles for resuspension into the atmosphere. The amounts of dust resuspended in this process are extremely difficult to predict or measure, as they depend critically upon factors such as the dust loading of the surface, the preceding dry period and the speed of moving traffic. However, the size distribution and chemical composition of particles in the urban atmosphere give a clear indication that this source can contribute significantly to the airborne particle loading of our cities.

3.6 Volcanic activities

These natural events may induce sporadically high PM_{10} levels in EU Member States; volcanic activity still occurs on some islands of continental Europe, such as the Canaries, Iceland and Sicily. Fine fly ash emitted from such volcanoes could represent an important local source of PM10 particles in nearby cities. Emissions of sulphur dioxide (SO_2) from volcanoes can also contribute to the formation of secondary particles. For instance, Mount Etna provides a semi-permanent emission of SO2 (4,000 tons/day) from volcanic plume and magma degassing.

3.7 Secondary Organic Biogenic Aerosols

Volatile organic compounds (VOCs) emitted from vegetation and their degradation products contribute to the organic fraction of secondary aerosol. They are emitted at considerable amounts: forests in Northern European regions cover a wide area, and naturally emitted terpenes highly contribute to gas-to-particle conversion. In these areas secondary aerosol (SOA) formation is an important source of fine particles also in environments otherwise free of primary sources; in the boreal forests of northern Europe, monoterpenes are abundant at concentrations ranging from some tens of parts per trillion up to parts per billion depending on season, boundary layer conditions, and temperature. European emission inventories (Simpson et al. 1999) revealed a total BioVOC release of 13 Tg per year. Total anthropogenic VOC emissions in Europe, assessed as 24 Tg per year, are distinctly higher. Emission inventories are based on models applied to calculate the BioVOC release from plant or vegetation type specific emission factors, leaf biomass, light and temperature data. When released into the atmosphere, monoterpenes undergo oxidation by ozone, hydroxyl radical, and nitrate radical to yield numerous compounds. These compounds may contribute considerably to the gas-to-particle conversion rate over forested areas.

For monoterpenes (C-10 hydrocarbons), oxygenated monoterpenes and isoprene, a C-5 hydrocarbon, a solid data base is available so that model outputs are quite reliable. Less is known about the quantity of emitted sesquiterpenes, semi-volatile C15- hydrocarbons, being more directly involved in particle formation processes than volatile C-5 to C-10 compounds. Upon pathogen attack and other plant stress factors sesquiterpene emission rates can increase by several orders of magnitude, so that total BioVOC emission model outputs have a high level of uncertainty: The secondary aerosol sources category “Biogenic VOC“ is estimated to account for 16 Tg VOCs per year on a global scale (IPCC 2001), but due to this uncertainty a range of 8

to 40 Tg is given. On the global scale 16% of the total organic fine aerosol may stem from BioVOC oxidation, a proportion accounting for about 1.6% of the total fine aerosol.

The BioVOC impact is relatively high in regions widely covered with forests, especially in Northern Europe (Tunved et al. 2006), where exceedences of PM limit values are rare. In areas relevant for EU legislation aiming at the improvement of air quality, the relative contribution of BioVOCs to total VOC emissions may be neglected. In Lombardy natural VOC emissions account only for 1.9% of the total VOC release, whereas 29% and 42% can be attributed to solvent use and road traffic, respectively (Carnevale & Volta 2006). Another fact underlining the minor relevance of BioVOC emissions at air pollution hot spots is that the major part of biogenic VOC is released during the warm months of the year, whereas exceedences of PM limit values occur predominantly in winter, when weather conditions favour the accumulation of pollutants over several days or weeks. The seasonality of BioVOC emissions results from the strong (exponential) increase of emission rates with increasing temperature.

4. Review of methods to quantify the natural component of PM

A number of methods for apportioning fractions of total PM to natural sources are available and some are implemented by certain Member States. The apportionment may be done using different methodologies: 1) using routine methods, 2) using information in parallel from background stations and 3) using advanced tools implemented by research groups.

However, the estimation of natural sources is quite difficult on the basis of measurements performed in monitoring networks, and only few Member States routinely implement methods for the identification and quantification of a natural episode.

Wind blown and long-range transported mineral dust and sea salt are the most important natural sources affecting particulate air quality in Europe, and available methods which make use of routine measurements and information from background stations currently refers generally to these two sources. The evaluation of any other contribution can at the moment be done only through advanced and expensive techniques.

4.1 Methods for the evaluation of natural events due to African dust

The impact of resuspended and transported African particulate matter from arid zones on atmospheric visibility and aerosol composition in more humid countries has been known for a long time.

Despite being a good tool for detecting the occurrence of African dust episodes, modeling alone cannot quantify the dust load of PM_{10} and $PM_{2.5}$. Methods applied for the quantification of dust events are in fact a combination of satellite imaging, modeling and background measurements data: the strength of the dust outbreaks over the Mediterranean tends to facilitate the Saharan dust detection by both ground and space based observations, allowing the quantification of its transport and of its optical and microphysical properties.

Dust outbreaks over the Mediterranean regions are often preceded by intense advections from Southwest Atlantic which induce low levels of suspended particles. Since mineral dust particles are of a relatively large size, a rapid and unexpected enhancement of PM_{10} levels in the network and in regional background stations may indicate the occurrence of a dust episode. The abrupt increase of the levels of particles registered in the air quality networks is caused by the rapid expansion of the African air mass related to an important pressure gradient between the Atlantic and the Mediterranean. These dust episodes may finish with red rains, which results in a rapid decrease of the levels of particles.

A further identification of dust incoming from Africa and the interpretation of the daily meteorological situations may come from the analysis of air mass backward trajectories using for example HYSPLIT model (Hybrid Single-Particles Lagrangian Integrated Trajectories).

The maps of TOMS (Total Ozone Mapping Spectrometer) aerosol index may also be consulted in order to evaluate the possible influence of Sahara/Sahel dust: the instrument can distinguish between different type of aerosol particles based on their size (dust tends to have larger particles than smoke) and absorbing properties in the UV. Other tools based on satellite of ground-base remote sensing freely accessible on the web are listed below:

- AERONET-AOT: a sun photometers ground based network providing aerosol optical thickness data
- SKIRON: regional weather forecasting system, operated by the University of Athens; predictions of dust loads (in mg/m^2)
- BCC-DREAM: dust prediction system of the Universitat Politecnica de Catalunya, providing daily dust forecasts (in g/m^2).

- NAAPs-NRL: predictions of optical thickness
- SEAWIFS: images on the ocean color
- MODIS: satellite images

These data may also allow the observation of a wide range of other phenomena such as forest fires and biomass burning.

When high PM_{10} levels are measured in regional background stations, the consultation of one of the above mentioned tools may confirm the influence of desert dust, verifying the origin of the dust plume.

Another feasible method for the evaluation and quantification of natural contribution to PM is routine monitoring through simultaneous measurements of PM_1 and PM_{10} concentrations. This methodology is based on the observation that mineral dust and seas salt are mainly (>90%) in the coarse fraction. Hence, an increase of the coarse-to-fine PM ratio may be indicative of a natural event.

Once a natural event has been identified, the nature of the event may be detected and quantified by chemical analysis of metals, ions and carbon compounds. Chemical mass balance analysis on the major component of PM_{10} may be performed during days exceeding limit values. Sahara or Sahel dust is made up of mineral particles which differ considerably, in composition and grain size, from anthropogenic particles. The chemical composition of dust particles reflects the composition of the sand that originated them, although heterogeneous reactions with anthropogenic pollutants can modify the original composition, either by nitrate or sulphate enrichment. Mineral dust particles are mainly composed of aluminum silicates, together with quartz and calcium- and magnesium carbonates. Therefore, only a minor fraction of the mineral dust is water soluble and can be analyzed, e.g., by means of ion chromatography, whereas other analytical methods, e.g. PIXE or XRF, permit to quantify the single elements regardless of their solubility.

Usually, an analysis showing enrichment in silicon, calcium, iron and aluminum in the aerosol indicates its geological origin. A number of studies for example demonstrated that nss-Ca^{2+} may be used as a tracer for crustal aerosol (Sciare *et al*, 1995, Putaud *et al*, 2004).

When the aerosol samples are subject to ion chromatography analysis, it is in fact convenient to use non-sea salt calcium as a tracer for the mineral dust. Three different equations used in literature to quantify the dust contribution to PM mass are reported following:

$$[dust] = [nssCa^{2+}] \times 10.9 \text{ (Gerasopoulos et al., 2006)}$$

$$[dust] = [nssCa^{2+}] \times 5.6 \text{ (Putaud et al., 2004)}$$

$$[dust] = [nssCa^{2+}] \times 15.0 \text{ (Putaud et al., 2004)}$$

These equations were derived by field campaigns and the variability of the gained factor underlines that the ratio of [dust] to [nssCa^{2+}] can vary according to the sampling locations or to the intensity of the dust advection event.

When elemental analysis data are available, the dust contribution can be quantified according to the metal-oxides abundance in the average earth soil composition, as proposed by Malm et al. (1994), for $PM_{2.5}$ samples:

[dust]=2.20[Al]+2.49[Si]+1.63[Ca]+2.42[Fe]+1.94[Ti] (Malm et al., 1994)

Two examples on how some Member States (Spain, Portugal and Italy in this case) are implementing methods for the evaluation and quantification of the contribution of Saharan dust (and sea-salt for method in 3.1.2) are described in the following paragraphs.

4.1.1 Identification of natural dust episodes affecting PM_{10} and $PM_{2.5}$ in Spain and Portugal

The following text shows a procedure to assign the African origin of the exceedences of the daily limit value of PM10 which has been applied in the air quality monitoring networks of Spain and Portugal.

The procedure can be summarized in the following tasks:

1. The research team formed by CSIC-UNL-INM-CIEMAT-UH, produces an annual report identifying African dust episodes based on:

1.1. Interpretation of the daily meteorological situations with the 5-day back-trajectories of the calculated daily air masses at 12h, for 750, 1500 and 2500 m.a.s.l (meters above sea level) using the HYSPLIT model (Hybrid Single-Particles Lagrangian Integrated Trajectories, version 4 Draxler and Rolph, 2003; http://www.arl.noaa.gov/ready/hysplit4.html), taking into account modelled vertical speed. The conclusions obtained from the analysis of back-trajectories are validated by means of the inspection of synoptic meteorological charts available in: http://www.ecmwf.int/ or http://europa.eu.int/comm/environment/air/pdf/finalwgreportes.pdf'

1.2. The maps of aerosol index of OMI that can be obtained in ftp://toms.gsfc.nasa.gov/pub/omi/images/aerosol/ are consulted. These maps reflect the indirect measurement of the OMI or Ozone Monitoring Instrument, which determines the total ozone column from the Ultraviolet radiation, and detects the seasonal variations. As the measurements

of ozone with this device are disturbed by the presence of absorbing aerosols, it is possible to extract other products in an indirect way, as the aerosol index. It is important to stand out that the OMI does not detect African dust events produced at surface level and therefore it is advisable also to check the daily images of the NASA satellite where this type of events are clearly visible. These maps can be obtained in: http://seawifs.gsfc.nasa.gov/cgibrs/seawifs_subreg.pl

1.3. The daily results of aerosol models outputs such as SKIRON (http://forecast.uoa.gr), DREAM (http://www.bsc.es/projects/earthscience/DREAM/) and NAAPs (http://www.nrlmry.navy.mil/aerosol/) are consulted.

1.4. INM executes HIRLAM model for obtaining wind fields at surface and height in order to identify possible contributions. It calculates 5-day isentropic back-trajectories data from the European Centre for Medium-Range Weather Forecasts (ECMWF).

1.5. The CSIC-UNL-INM-CIEMAT-UH research team produces periodically reports on the 24 h forecast of dust outbreaks (e-mail alerts sent to air quality networks 24h in advance) and on a list of dates with validated occurrence of African dust outbreaks since the beginning of each year. In parallel, the research team receives daily information on the levels of PM measured at regional background stations from air quality monitoring network that are presented in Figure 7 and Table 2, recording the levels of PM with real time equipment (for example beta attenuation or oscillating microbalance TEOM). Many of them are also equipped with manual instrumentation which is used for the validation and correction of data from automatic monitors. The following stations compose this monitoring network: EMEP-CAMP-VAG network (4), private Spanish networks (4), Andalusia (3), Catalonia (1), Euskadi (4), Cantabria (1), Balearic (1), Community of Valencia (1), Portugal-Peninsula (4), Canary islands (4) and Madeira islands (1). In a considerable part of these cases it would be possible to have PM_{10} data in real time. The data of the rest of the stations, presented in Figure 7 and Table 2, are used in a final stage to validate the episodes with corrected real time measurements or gravimetric measurements of PM_{10}. The result of these tasks is the production of tables containing the compilation of the levels of PM_{10} registered in the mentioned regional background stations, with the indication of the days in which there has been influence of African dust contributions. This is sent to the air quality monitoring networks after the detection of each African episode. High PM_{10} levels registered in regional background stations with an advance of one day or a delay of two days with respect to the resulting dates of the study of detection of African dust episodes, may be considered within the episode (tasks 1.1. to 1.4). This occurs

when the African air masses transported onto the Iberian Peninsula are not followed by episodes of intense Atlantic advection that renew the regional air masses. Tthen the African dust in suspension has a higher time of residence during which the PM_{10} levels remain high. Studies made in this sense show that this after-effect (or indirect) on the PM_{10} levels usually lasts between 1 or 2 days once stopped the advection of African air masses on the peninsula (see additional justification at the end of the procedure).

1.6. In order to quantify the regional background levels of PM_{10} for a day of African dust influence (not all the PM_{10} mass arises from the African dust outbreak), in each time series of the station of the corresponding regional background, the percentile 30 of the moving averaged monthly means of every day of measurement is determined. In this procedure, the day in evaluation is taken as the central day of the monthly period of 30 days. Studies made on the levels of PM_{10} registered in EMEP stations of Spain during episodes of Atlantic advection (with low external contributions of PM on the peninsula) by Escudero (2006) show that percentile 30 reproduces rather suitably the registered regional background during advective processes. At the end of this report the selection of the 30 percentile is technically supported. The value corresponding to this monthly daily mean moving percentile is subtracted from the daily average of PM_{10} determined in the station of regional background for every day affected by the African contribution. With this the daily net dust load in PM_{10} is obtained.

1.7. The information provided in sub-tasks 1.1 to 1.6 is added to the tables previously mentioned for the coincident days with episodes of African PM_{10}, the daily values of net dust load in PM_{10} registered in regional background stations.

1.8. A complete report is produce at the end of year (with delivery to air quality networks within the three first months of the following year), justifying and describing in detail each one of the episodes of PM_{10} attributed to African dust contributions for each zone shown in Figure 8. The tables of daily levels of PM_{10} registered in stations of regional background once validated and corrected by means of the factors obtained from the intercomparison of manual and automatic equipment or by the manual measurements, where possible, are enclosed. Finally, the values of the daily net African dust load determined by means of the procedure exposed in 1.6 based on the definitive levels of PM_{10} are also enclosed. This table is the base for the discount of exceedences due to natural contributions. Independently, the e-mail alerts and the non-definitive tables of episodes and levels for each episode are being sent to the air quality networks.

2. The air quality monitoring networks provide a comprehensive inventory of the days with exceedences of the PM_{10} daily limit value for each monitoring station. In addition, the list of dates with the identification of African episodes provided by the CSIC-UNL-INM-CIEMAT-UH research team at the end of year is compared (sub-task 1.8), and is obtained a list of days with exceedences that correspond with African episodes.

3. The air quality monitoring networks compare PM_{10} levels registered for each overcoming and for each station of the network with those registered simultaneously in the regional background stations, which are provided in individual tables incorporated in the annual Report of the CSIC-UNL-INM-CIEMAT-UH research team (sub-task 1.8).

4. For those days in which the daily limit value is surpassed in a station of urban or industrial type and in which it has been identified an episode of African particle contribution (as reported by CSIC-UNL-INM-CIEMAT-UH in sub-task 1.8) a subtraction of the daily net African dust load determined in the corresponding regional background station (close to the network at issue) is made. If the result of this subtraction is lower than the daily limit value, it can consider that this overcoming is attributable to the natural contribution in the considered station, and therefore can be discounted. For example: In two stations of urban background and traffic, 60 and 100 are registered $\mu g/m^3$, respectively, during a specific day in which the report indicates that an African air mass intrusion has taken place. In the regional background station close to the mentioned stations, a daily value of PM_{10} of 41 $\mu g/m^3$ is registered simultaneously and the monthly percentile 30% for that day reaches 10 $\mu g/m^3$. Therefore the net African dust load in this regional background station, and therefore in the region, is of 41-10=31 $\mu g/m^3$. In this case the overcoming registered in the urban background station should be discounted (60-31= 29 $\mu gPM10/m^3$ <50 $\mu gPM10/m^3$), but not in the traffic one (100-31= 69 $\mu gPM10/m^3$ >50 $\mu gPM10/m^3$).

It may occur that air mass with high African dust load contains greater concentrations at certain heights. Since many of the selected stations of reference in sub-task 1.6 are located at higher heights than the closed urban networks, in the mentioned cases they can register higher levels of PM10 than certain stations of reference with respect to the urban ones. Therefore when subtracting the net African dust load, negative values would be obtained. In these cases the net dust load should be calculated averaging the African contributions obtained in the reference regional background station and in the closest regional background station, apart from the reference one. If still the difference results in a negative value the total amount of PM10 must be eliminated because it is supposed that the mineral dust contribution from African

sources to the levels of PM10 in the urban station should be dominant with respect to the anthropogenic contribution. The exposed problem is attributed to the limitation of representativeness of the data from the reference stations, and it must be assumed - to locate reference stations very near each one of the measurement networks, it would be an extremely expensive strategy and in addition, the reference stations would be seen in many cases influenced by the urban emissions.

5. **The air quality monitoring networks** provides a list of total exceedences (caused by African dust and non-African episodes), and another list identifying those exceedences that fulfil the requirementsdescribed in the previous section, and consequently interpreted as caused by the natural dust outbreak. Also, the annual average of PM_{10} should be calculated with and without considering the levels of the days with exceedences of the limit value of PM_{10} caused by African episodes. In the late case, the daily mean values for days with exceedences caused by African dust outbreaks will not be taken into account for the calculation of the annual average. The difference between both is identified as the annual contribution of African mineral dust to the mean levels of PM_{10}. Thus, the final information to be supplied to the Ministry of the environment is: a) The original mean annual average of PM_{10}, b) The total number and the list of annual exceedences of the daily limit value, c) a separate list with the identification of exceedences caused by natural episodes; and d) the calculated African dust contribution to the mean annual PM_{10} levels.

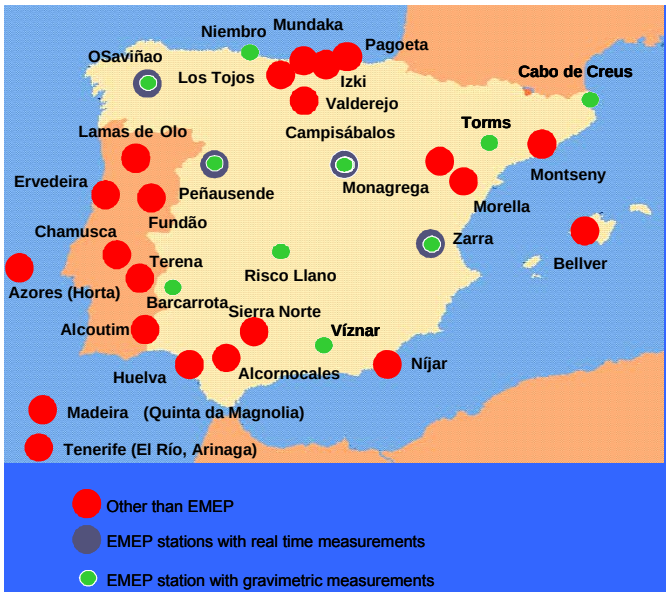


Figure 1. Regional background stations network used for detection of African dust episodes.

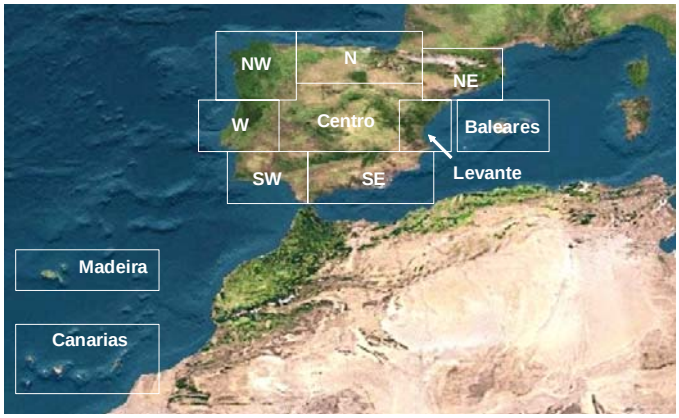


Figure 2. Zones considered for the identification of contributions of African dust episodes to PM10. The Canary Islands; Madeira islands; Southwest: Western, South Andalusia of Extremadura, Algarve (Portugal); Southeastern: Eastern Andalusia, Murcia; The East: Valencian community until Ebro delta; The west: Central zone Portugal; Center: Extremadura rest, Castile Mancha, Community of Madrid, Leon Castile; The northwest: Galicia, Asturias, the Northwest Castilla and Leon, North of Portugal; North: Cantabria, Basque Country, Navarra, Rioja; The northeast: Aragon, Catalonia.

Table 1. Network of regional background stations to use for detection of African episodes.

NW Península			
O Saviñao	43º 13' 52"N	7º 41' 59"W	506 m.a.s.l.
Lamas de Olo	41º 18' 37"N	7º 45' 02"W	1086 m.a.s.l.
W Península			
Fundão	40º 07' 48"N	7º 29' 24"W	473 m.a.s.l.
Chamusca	39º 21' 05"N	8º 28' 23"W	43 m.a.s.l.
Ervedeira			32 m.a.s.l.
Terena	38º 36' 54"N	7º 23' 51" W	187 m.a.s.l.
SW Península			
Barcarrota	38º 28' 33"N	6º 55' 22"W	393 m.a.s.l.
Alcoutim	37º 26' 51"N	7º 27' 35"W	300 m.a.s.l.
Doñana	37º 11' 23"N	6º 31' 21"W	
S y SE Península			
Viznar	37º 14' 00"N	03º 32' 00"W	1265 m.a.s.l.
Níjar	36º 58' 01"N	02º 11' 59"W	
Sierra Norte	38º 06' 20"N	05º 49' 48"W	801 m.a.s.l.
Alcornocales	36º 21' 00"N	05º 32' 00"W	
N Península			
Niembro	43º 26' 32"N	04º 51' 01"W	134 m.a.s.l.
Valderejo	42º 52´ 31´´N	03º 13´ 53´´W	911 m.a.s.l.
Izki	43º 19´ 05´´N	03º 01´ 58´´W	830 m.a.s.l.
Mundaka	43º 24´ 22´´N	02º 42' 14´´W	116 m.a.s.l.
Pagoeta	43º 15´ 02´´N	02º 09´ 18´´W	215 m.a.s.l..
Los Tojos	43º 09' 03"N	04º 14' 51"W	

Center Península			
Campisabalos	41º 16' 52"N	3º 08' 34"W	1360 m.a.s.l.
Peñausende	41º 17' 00"N	5º 52' 00"W	985 m.a.s.l.
Risco Llano	39º 31' 00"N	04º 21' 00"W	1241 m.a.s.l.
E Península			
Morella	40º 38' 10"N	00º 05' 32"W	1153 m.a.s.l.
Zarra	39º 05' 10"N	01º 06' 07"W	885 m.a.s.l.
NE Península			
Els Torms	41º 24' 00"N	00º 43' 00"E	470 m.a.s.l.
Monagrega	40º 56' 45"N	00º 16' 15"E	
Montseny	41º 46' 47"N	02º 22' 40"E	730 m.a.s.l.
Cabo de Creus	42º 19' 10"N	03º 19' 01"E	23 m.a.s.l.
Baleares			
Castillo de Bellver	39º 33´ 50´´N	02º 37´ 22´´E	113 m.a.s.l.
Canarias			
Estaciones primarias:			
El Río (TF)	28º 08' 42"N	16º 31' 25"W	500 m.a.s.l..
Arinaga (GC)	27º 52' 09"N	15º 23' 13"W	23 m.a.s.l..
Madeira islands			
Quinta da Magnolia	32º 44' 44"N	16º 58' 28"W	
Stations to be used in case of data absence:			
Buzanada (TF)	28º 04' 21"N	16º 39'10"W	308 m.a.s.l..
Sardina (GC)	27º 50' 54"N	15º 28' 03"W	158 m.a.s.l..
Horta (Azores)	38º 36' 18"N	28º 37' 53"W	310 m.a.s.l.

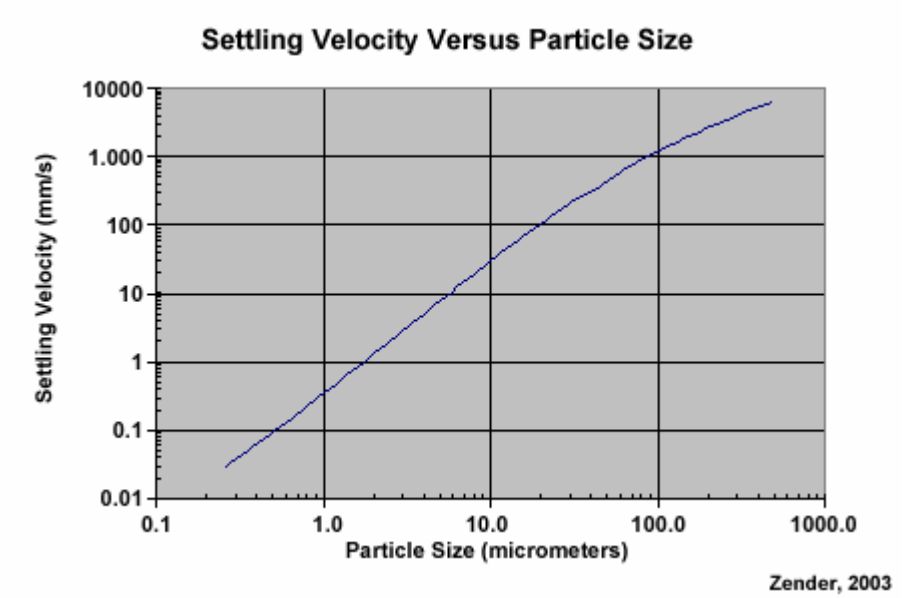
Additional justification of the persistence of some African episodes

In certain cases in which incursions of masses of African dust occur over Europe, PM_{10} levels can be affected by these natural episodes during the days (1 or 2 days) after the last day in which the retro-trajectories indicate the existence of the episode. This is due to:

a) When the African air masses are transported over Europe, these are not always followed by episodes of intense Atlantic advection that renew the regional air masses,so that the African dust in has a higher time of residence during which it noticeably affects PM_{10} levels;

b) These African air mass intrusions developed vertically. According to several authors (De Tomasi, 2003; Alpert et al., 2004; Balis et al., 2004; Perez, C., 2005) during all the scenarios of transport of African air masses towards the Iberian Peninsula dust reaches a minimum altitude of 1500 m over sea level. If we consider that the particles of 1 to 10 μm have an average deposition velocity of 0.6 cm/s (see figure of Zender et al., 2003), this means that:

0.6 cm/s=36 cm/min=21.6 m/h=518.4 m/day



http://meted.ucar.edu/mesoprim/dust/print.htm

This means that in approximately 3 days the particulate matter that has travelled to about 1500 m will fall out. In the centre of the Iberian Peninsula (with an average altitude of 500m) this material would need around 2 days to deposit once the intrusion finished.

Justification of the selection of percentile 30

In order to discount the levels of PM_{10} contributed by the regional background of the zone, for a day of African influence, in each series of a station of corresponding regional background the monthly moving **percentile 30** is determined for each day. The day in evaluation is taken as the central day of the monthly period of 30 days. Studies made on the levels of PM10 registered in stations EMEP of Spain during episodes of Atlantic advection (with low external contributions of PM on the peninsula) by Escudero (2006) show that percentile 30 reproduces rather suitably the background levels. Thus, in the attached Table 3 and Figure 9 it is possible to observe that the mentioned percentile 30 reproduces quite reasonably the mean levels registered for days with Atlantic advection in stations EMEP and other stations of regional background of Spain.

Correlation between levels corresponding to percentiles 10, 20 and 30 of the daily mean levels of PM10 during 2004 and 2005 in stations of regional background of Spain (including stations EMEP), with the mean levels corresponding to days exclusively of Atlantic advection according

to analysis of Escudero (2006). Percentiles 10 and 20 underestimate the Atlantic advection levels slightly.

Table 2. PM_{10} mean levels in EMEP and other regional background stations during episodes of advection of Atlantic air masses.

	Zarra	Viznar	Els Torms	Cabo de Creus	Monagrega	Montseny	O Saviñao	Barcarrota	Niembro	Izkis	Valderejo	Peñausende	Campisábalos	Riscollano
Adv ATL	11	13	13	18	12	17	10	13	16	10	10	8	7	8
Adv MED	10	16	15	24	11	15	17	15	16	11	12	13	9	10
P10	8	10	10	13	8	8	6	9	9	6	8	6	5	6
P20	9	13	12	15	10	10	8	11	11	7	9	7	6	8
P30	11	15	14	16	12	12	9	13	12	8	10	8	7	9

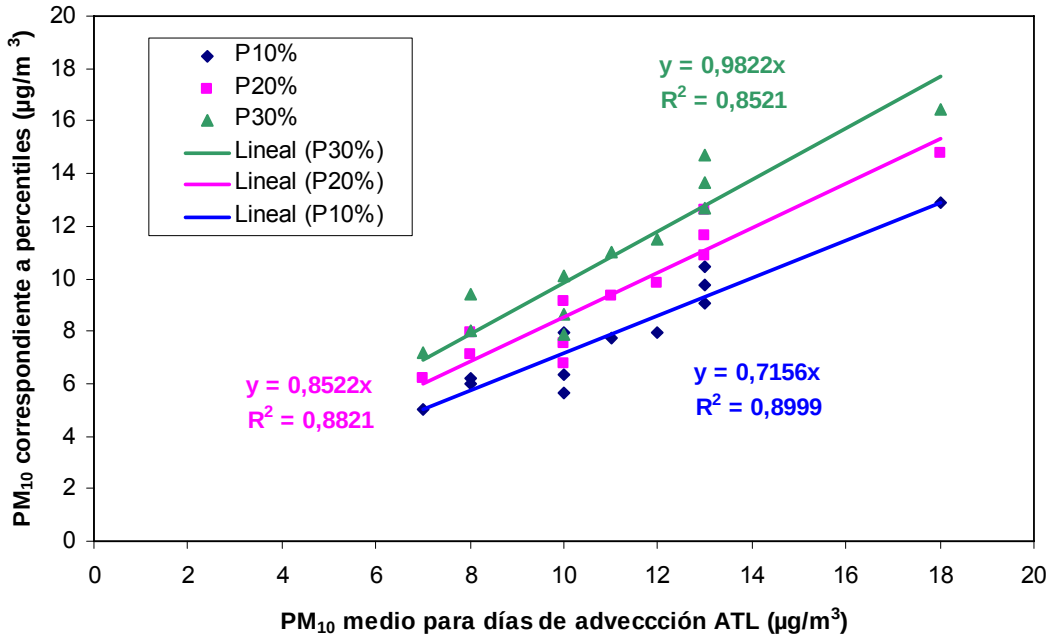


Figure 3. Correlation between the mean PM_{10} for days with Atlantic advection and the mean levels of the monthly 30th percentile levels in EMEP and other regional background stations.

Other considerations:

a) When simultaneous variations of the levels of PM_{10} are registered in all the stations of a network of air quality monitoring it can be due to:

• an external contribution that affects all of them

• meteorological conditions (stagnation, dispersive conditions, precipitation) that favours simultaneously the accumulation of local pollutants)

• anthropogenic emissions, with simultaneous emission spectrum, for example the sequences of weekly emissions of traffic (low levels in week ends and high during the week).

All of this the exceedences of the daily limit value must only be attributed to external contributions if there is a previous demonstration (sub-tasks 1.1 to 1.6).

b) The use of a reference station can be replaced by the accomplishment of a chemical balance of masses of the majority components of PM10 for the days that surpass the limit value. Since the particulate material of the Sahara/Sahel is mainly constituted by quartz, calcite, dolomita and clay minerals, the direct analysis of Ca, Al_2O_3, Fe_2O_3, K, Mg, and the indirect determination of Si ($3*Al_2O_3 = SiO_2$)) and CO_3^{2-}($1.5*Ca + 2.5*Mg = CO_3^2$ allows the determination of the mineral load contributed by the Sahara. If this load is extracted of the total of PM10 and it not surpasses the limit value is possible to be deduced that the natural contribution is responsible for the overcoming. This procedure is much more expensive, and in addition it is put under the mineral dust interference coming from other anthropogenic sources (Querol et al., 2001 and 2004b and c), therefore in case of being applied would have to be only made for days in which African contribution in sub-tasks 1.1 to 1.6 has been identified.

c) The atmospheric particles in suspension in the arid and semi-arid areas in the south Europe have a greater mineral load when it is compared with the countries of central and Northern Europe. This characteristic is not exclusive of Europe since a great number of studies have demonstrated a similar differentiation between the East and West coasts of the United States. The greater mineral contribution to aerosol levels in arid and semi-arid areas is attributed to:

a) The absence of vegetal cover of the ground favours the resuspension of soil particles.
b) The low volume of precipitation diminishes the washing out of particulate matter.
c) Intense atmospheric convective dynamics (induced by the high insolation), frequent in spring and summer, favours the resuspension.

Since the physico-chemical characteristics of resuspended natural particles differ clearly from anthropogenic particles, in most of the situations, physical and chemical measurements allow the identification of high particle levels events induced by processes of local resuspension.

In case of doubtful processes of local resuspension that can increase levels of PM10 in a certain control station, it is recommended to carry out a chemical balance of masses. This analysis must be performed during a minimum of a year (approximately 75 distributed daily

samples homogenous throughout the year) to determine the periods of influence and to obtain the proportion of natural material in the PM10 levels. The direct analysis of Ca, Al_2O_3, Fe_2O_3, K, Mg, Ti, and P and the indirect determination of Si ($3*Al_2O_3 = SiO_2$)) and CO_3^{2-}($1.5*Ca + 2.5*Mg = CO_3^{2-}$) allow the determination of the mineral load. If, after making the extraction of this load of the total concentration of PM10, the value does not exceed PM10 limit, it can be deduce that the natural contribution is responsible for the exceedance. In urban background stations, the levels of SO_4^{2-}, NO_3^-, NH_4^+ and not mineral C (C of organic origin) would represent the anthropogenic load, whereas levels Cl^-, Na^+, the marine SO_4^{2-} and Mg^{2+} (both determining indirectly from the levels of Na+) would represent the load of marine aerosol.

Once the importance of the contribution of particulate material by resuspension has been demonstrated by means of analysis of contribution of sources, the following procedure to identify the resuspension events is proposed to be applied:

1. Identify exceedences of the limit values of daily PM10 of the directive (PM10>50 $\mu g/m^3$).

2. Compile the information of time series obtained simultaneously in different stations from the monitoring network and in a rural station (EMEP as reference) near the control area.

3. Compare the time series of PM10 obtained during each overcoming of the limit PM10 levels and elaborate a list with the peaks of PM10 registered simultaneously in the considered stations. The lower concentrations of anthropogenic particulates are more probable in spring and summer that in autumn and winter due to the conditions of greater atmospheric dispersion and to the smaller ratios of emission. Therefore, the high events of PM10 that take place in spring and summer can have a greater natural contribution than those that take place in winter.

4. Make simultaneous measures of the levels of PM10 and PM2.5 in one of the control stations and in the area of reference. The mineral fraction of resuspended soil particles is concentrated mainly in the coarse fraction (>2.5 microns). Therefore, in the case of high events of PM10 registered simultaneously in the control and reference stations, if the proportion of PM2.5 in PM10 or PST is low (< 50% in weight), the resuspension processes is possibly responsible for the high levels of PM10. However, it is necessary to review, that is due to demonstrate the absence of sources of primary particulate emission (ceramic, mining, cement) in the zone, since this type of anthropogenic sources mainly emits concentrated particles in the rank between 2.5 and 10 microns.

4.1.2 Contribution of Natural Sources to PM in central Italy

The method adopted by the Italian National reference Laboratory of the CNR – Institute of Atmospheric Pollution in Rome is a 3-step procedure.

A) The mixing properties of the lower boundary layer are initially evaluated by means of natural radioactivity (radon progeny) concentration measurements; starting from natural radioactivity values, Atmospheric Stability Indexes can be developed, which give for each day the probability, from the meteorological point of view, for the occurrence of an atmospheric pollution event. (Fig.4)

Fig. 4: Example of modeled PM_{10} values (green line) based on Atmospheric Stability Index calculation in comparison with measured values (red line) in an urban background station in Rome (Italy). (Courtesy of Perrino and Allegrini., presented at Workshop on "Contribution of natural sources to PM levels in Europe"JRC ISPRA, October 2006)

The temporal trend of natural radioactivity is in general characterized by low values during day-time (convective mixing of the atmosphere) and maximum values during night-time (atmospheric stability and accumulation of Radon). The mixing properties of the lower atmosphere are a key factor in determining PM concentration levels: in the case of natural events (e.g. desert dust intrusion) the values of the Atmospheric Stability Index do not match with measured PM_{10} concentrations and an increase in PM_{10} during advection condition is experienced (Fig.5).

Fig.5: Experimental and modeled PM10 values during a Saharan dust episode in an urban background station in Rome (Italy) (Courtesy of Perrino and Allegrini, presented at Workshop on "Contribution of natural sources to PM levels in Europe" JRC ISPRA, October 2006)

B) The daily average ratio between the number of particles in the coarse (>1.5 μm) to the fine (0.3 – 0.5 μm) ranges is evaluated: an increase of this ratio indicates that a natural event is occurring.

Fig.6: Ratio between coarse to fine fraction measured with an OPC in an urban background station in Rome (Italy) (Courtesy of Perrino and Allegrini, presented at Workshop on "Contribution of natural sources to PM levels in Europe" JRC ISPRA, October 2006)

C) The further chemical characterization of particles with the analysis of metals, ions and carbon compounds, allows the identification of the main sources (Fig. 7), in particular of sea-spray and crustal materials defined as:

$$[\text{sea-spray aerosol}] = (Na^{+} + Cl^{-}) * 1.176$$

$$[\text{crustal}] = (1.89\ Al + 2.14\ Si + 1.4\ Ca + 1.2\ K + 1.36\ Fe) * 1.12$$

Fig. 7: Increase of the crustal fraction during a Saharan event detected by chemical analysis of the macro-components (Courtesy of Perrino and Allegrini, presented at Workshop on "Contribution of natural sources to PM levels in Europe"JRC ISPRA, October 2006)

Natural events can be identified from an increase of the coarse-to-fine ratio, and the nature of the event is detected by chemical analysis, as indicated as an example in Fig. 8.

Fig. 8: Identification of a natural event by means of coarse-to-fine PM ratio evaluation and chemical characterization of the origin of the event (Courtesy of Perrino and Allegrini, presented at Workshop on "Contribution of natural sources to PM levels in Europe" JRC ISPRA, October 2006)

4.2 Methods for the evaluation of sea-salt contribution to PM

A means to calculate the sea salt contribution is to rely on the average sea water composition, which is reported in Table 3, and on inorganic ions speciation in the collected aerosol samples, together with an air mass back trajectories evaluation.

chemical ion	valence	concentration ppm, mg/kg	% by weight	molecular weight	µmol/ kg
Chloride Cl	-1	19345	55.03	35.453	546
Sodium Na	+1	10752	30.59	22.990	468
Sulfate SO_4	-2	2701	7.68	96.062	28.1
Magnesium Mg	+2	1295	3.68	24.305	53.3
Calcium Ca	+2	416	1.18	40.078	10.4
Potassium K	+1	390	1.11	39.098	9.97
Bicarbonate HCO_3	-1	145	0.41	61.016	2.34
Bromide Br	-1	66	0.19	79.904	0.83
Borate BO_3	-3	27	0.08	58.808	0.46
Strontium Sr	+2	13	0.04	87.620	0.091
Fluoride F	-1	1	0.003	18.998	0.068

Table 3: Salt ions in sea water

Chloride, sodium, sulphate, magnesium, calcium and potassium are the major ions in the aerosol samples and are routinely analyzed by means of, e.g., ion chromatography. Considering Na as entirely of primary marine origin (the air mass back trajectories can help to evaluate if this assumption is correct), the sea salt fraction of the other ions can be calculated according to the ratios between Na and the other ions in the sea water, as e.g. for sea salt sulphate ($ssSO_4^{=}$):

$$\left[ssSO_4^{=}\right] = \left[Na^{+}\right] \times \frac{7.68}{30.59}$$

where [Na^+] is the measured sodium concentration (e.g. in ppm or µg/m³) and [$ssSO_4^=$] is the sulphate concentration due to the sea salt contribution; 7.68 and 30.59 are the percentage contributions of sulphate and sodium to the salinity of sea water. Likewise, the sea salt contribution for every ion can be calculated according to the percentages reported in Table 3. The sum of the [ss-Ions] is the contribution of sea salt to the PM loading.

In theory, also chloride could be used as a reference ion to calculate the sea salt contribution (see 2.2.1, Dutch procedure), but the samples can be subjected to chloride depletion due to the reaction with HNO_3 or H_2SO_4, as reported below:

$$NaCl_{(solid)} + HNO_{3(gas)} \rightarrow NaNO_{3(solid)} + HCl_{(gas)}$$
$$2NaCl_{(solid)} + H_2SO_{4(gas)} \rightarrow Na_2SO_{4(solid)} + 2HCl_{(gas)}$$

Therefore the use of sodium is preferable.

The non-sea salt component of the ion can be calculated by subtracting the sea salt fraction from the total ion concentration, e.g.:

[$nssSO_4^=$] = [$SO_4^=$] - [$ssSO_4^=$]

Simpler and widely used methods to calculate the sea salt contribution consider only one coefficient and multiply it by the measured concentration of sodium or chloride. The coefficients are calculated assuming that sea salt is made only by NaCl and that all Na and Cl are associated in sodium chloride. Therefore, according to the sea water composition:

$$[\text{Sea salt}] = 100/55 \times [Cl] = 1.8 \times Cl$$

or

$$[\text{Sea salt}] = 2.54 \times [Na]$$

or

$$[\text{Sea salt}] = ([Na^+] + [Cl^-]) \times 1.176$$

The same considerations made in 2.1 about the possibility to identify a dust episode by means of the evaluation of the coarse (PM_{10}) to fine (PM_1) ratio are valid also for marine aerosol; it has been in fact proven that more than 90% of sea-salt concentration is in the coarse fraction.

Some examples showing the applicability of the methods described for the evaluation of sea-salt contribution are illustrated in the following sections.

4.2.1 Evaluation of sea-salt contribution to PM_{10} in The Netherlands

In 2005, Dutch legislation permitted the possibility to correct ambient PM10 concentrations for the contribution of natural sources without adverse health effects.The National Institute for Public Health and the Environment (RIVM) of The Netherlands defined a methodology to quantify the sea salt contribution.

To set up the methodology, four stations were chosen as sampling locations and daily average PM_{10} values and Chloride concentrations in PM_3 were measured.

The amount of sea salt in PM10 was estimated as:

$$PM_{10} \text{ sea salt} = [Cl^-] \times a \times b \times c$$

Where

a= 1.8 (according to the sea water composition);

b= sea salt PM_{10}/ sea salt PM_3 =3 ± 1

c=1.25 ± 0.15, accounting for chlorine depletion mainly caused by reaction with HNO_3 (ca. 20%)

The uncertainties of the methodology are associated with the “b” and “c” coefficients, and range from ca. 2 to ca. 6, as reported below:

low: $b*c = 2*1.10 \approx 2$

median: $b*c = 3*1.25 = 3.75$

high: $b*c = 4*1.40 \approx 6$

Within uncertainty, results were consistent with several short term measurement series of Na^+, thus proving the validity of the methodology.

Sea-salt contribution was then evaluated in five different locations for the period 2000-2003, and the average number of days per year where limit values for PM_{10} were exceeded due to sea-salt contribution was therefore calculated.

The average number of days calculated for different b x c values are reported below:

b x c		average number of exceedences caused by sea salt (days)
low	≈2	4
median	=3.75	6
high	≈6	8

On average a reduction of 6 exceeding days is calculated for the most likely value of the parameters b*c. A range of 4 to 8 days is found as average for the 2 extreme values of b*c. No relation was found between location and number of days with high PM10 values caused by sea salt contribution, most probably due to the limited amount of data, and therefore the Ministry decided that the subtraction of 6 days is permitted for model calculations made by municipalities on every location in The Netherlands.

It seems rather contradictory that the reduction of exceeding days is equal while the annual average shows a strong gradient over the country. The explanation for this phenomenon is that exceeding days usually occur with continental (south to east) wind directions and the high sea salt concentrations on sea (west) wind directions.

The uncertainty in both the reduction in exceeding days and in the estimated annual average is approximated as 50 %. Thus, future work on the methodology will focus on the reduction of the uncertainty, e.g. considering $[Na^+]$ and $[Mg^{2+}]$ directly measured on PM_{10} samples instead of $[Cl^-]$ measured on PM_3 samples.

4.2.2 Sea-salt evaluation during a measuring campaign in Milan

The analysis of the chemical composition of the aerosol coupled with the evaluation of the air mass backward trajectories is in many cases a good tool for the identification of a natural event.

As an example results from a JRC measuring campaign in the area of Milan (July 2006) are shown. Ion chromatographic measurements evidenced during two days an unexpectedly high concentration in the coarse fraction (PM_{1-10}) of sodium chloride and sulfate, and an elevated level of nitrate compared to the other days of the campaign (Fig.9).

Figure 9: Atmospheric concentrations (above) and percentage chemical composition (below) of the fine (PM_1) and coarse (PM_{1-10}) water soluble inorganic aerosol fraction during a summer campaign in Milan (Marelli, Emblico et al., 2006, unpublished data)

In order to confirm the suitability of this potential marine fingerprint, back-trajectories analysis of air masses was performed. While in the first period the air masses reached the sampling location from the north, during the days of high sodium chloride, sulfate and ammonium concentration, an easterly air mass advection occurred from the northern Adriatic Sea, inducing a modification in the chemical composition of the coarse fraction of the aerosol with a contribution of sea-salt (Fig.10)

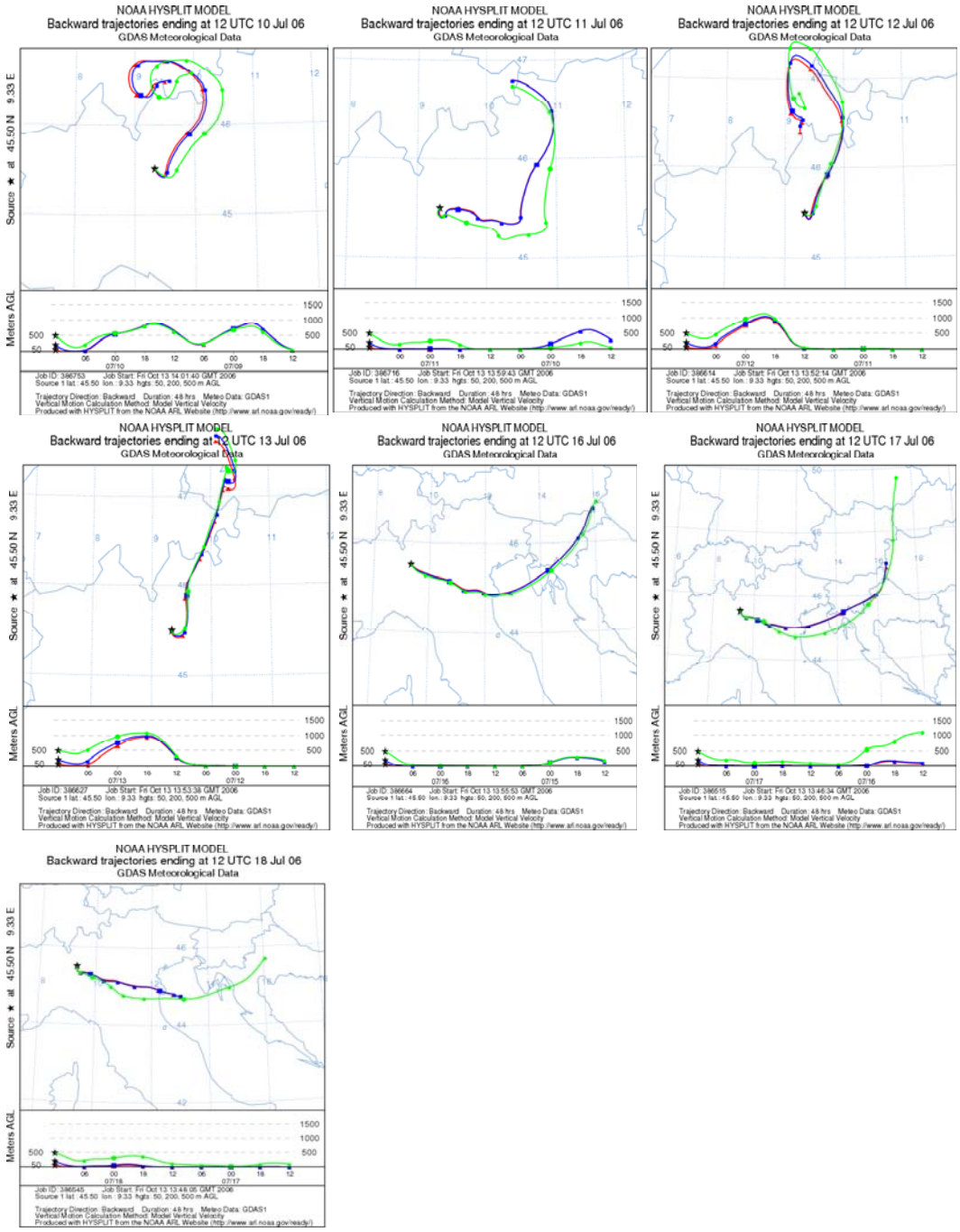


Fig. 10: 48 hours back trajectories for July 10-18th (Marelli and Emblico et al., 2006, unpublished data)

4.3 Methods for the evaluation of PBAP

Quantification of fractionated material of PBAPs is difficult, as neither structure nor size are well defined. Guidance to which particles are to be considered PBAPs is given by their composition. A comprehensive approach to cover PBAPs quantitatively has been taken by Matthias Maser et

al. (2000). They use protein as a tracer compound. With this method, they collect information on PBAPs generally. More specific analyses have been developed by Kunit and Puxbaum (1996) who focus on the determination of cellulose only. Cellulose will be a compound contained in fractionated plant tissue, or plant debris, but also in fractionated pollen, but it will not include fungal material or material from animals.

In the following, the evaluation will be focused on the mass fraction of PBAPs to PM_{10} concentration, in order to better understand their contribution to particulate air pollution. Among the individual units, fungal spores will be only considered, since they are the most relevant in terms of PM_{10} mass. All of the other PBAPs may be considered to be covered by plant debris identified by its cellulose content.

4.3.1 Plant Debris

Plant material contains cellulose as structural element. Measurements of atmospheric concentrations of cellulose are available from a handful of sites in Europe (Sanchez Ochoa, 2005). No emission fluxes are available, as also the emitting process is not readily defined. It may be assumed that different fractions of plant material are broken up by mechanical and/or decay processes, and the resulting particles become airborne due to air movements (wind, but also a passing vehicle).

Atmospheric concentrations may be compared to those ones of other compounds, for which the emission fluxes are known. The ratio of concentration should then – if the atmospheric behaviour is sufficiently similar – be equal to the ratio of emission flux.

In the case of cellulose measurements, concurrent measurements of levoglucosan have been performed (Puxbaum et al., 2006). Levoglucosan is a tracer for wood fire. Atmospheric woodsmoke concentration can be derived from levoglucosan measurements, based on measured conversion rates of wood lignin during combustion (Fine et al., 2002). Likewise organic matter concentrations of plant debris from measured cellulose may be assessed (Kunit and Puxbaum, 1996). Assuming that both compounds are sufficiently conservative and experience the same atmospheric dispersion, their atmospheric concentration ratio may be expected to correspond to the ratio of their emission fluxes. As wood fire emissions are available at a country scale (IIASA, 2005), results of the cellulose measurements mentioned above are presented at that scale (Tab. 4). In order to derive an emission factor, the country emissions are related to an area considered relevant for such emissions (total area, without “barren land” and “water area” – land use information taken from a CORINE reclassification: R.

Koeble, personal information). Total area is also attempted, and forest area as proxy, but in one case it did just not seem plausible to have a no-vegetation area and assign it for emissions, and in the other case detailed speciation just did not seem justified by the available data.

site	country	Wood smoke measured (ng/m^3)	Plant debris measured (ng/m^3)	PM10 emissions from wood combustion [kton/yr]	Relevant area [km^2]	Emission factor plant debris [$kg/km^2/yr$]
Azores	Portugal	Background site – no relevant emission area available				
Aveiro	Portugal	4930	104	21	86157	5.02
Puy de Dome	France	162	120	122	538369	167.4
Schauinsland	Germany	233	178	17	355796	37.1
Sonnblick	Austria	Background site – no relevant emission area available				
K-Puszta	Hungary	2953	266	6	91497	5.86

Tab. 4: Assessing an emission factor for plant debris emissions.[concentration data from the CARBOSOL project, Sanchez Ochoa, 2005, and Puxbaum et al., 2006, respectively; emissions from IIASA, 2005]

The emission factors derived exhibit a considerable range. Two sites had to be excluded immediately, as the method applied requires that the area the emission estimate derives from the requirements to have at least some influence on the measured concentration. Portuguese emissions hardly influence the atmosphere of the Azores, and it is also virtually impossible to identify the relevant emission area for Mt. Sonnblick. Possibly a similar situation occurs for Puy de Dome, a site in the French Massive Central close to forests but distant to anthropogenic activities: plumes from wood fires then reach the site to a much lesser extent than plant debris emissions. The same may also be the case for the German site, even if less pronounced – especially as one may expect situations strongly different in different parts of that large country. The selection of a definite emission factor is thus mostly influenced by the sites in small countries. The suggested factor of 6 $kg/km^2/yr$ may be seen as a conservative low estimate.

A critical assumption for this approach is the representativity of the site with respect to national emission data. Simpson et al. (2006) use basically the same data for the identical measurement sites and try to understand measured levoglucosan concentrations from emission data applying the EMEP chemical transport model. Their model results differ from the measurements by about

a factor of ten, for those sites that were considered most useful her. One possible reason (additionally to errors in emission modelling or measurements) might be inadequate representation of spatial distribution of emissions, i.e. that wood combustion dominates much more strongly for the measurement site than in the Portuguese average. In that case, the emission factor proposed for plant debris would have to be corrected to be ten times as high. But at this time also alternative explanations are possible, e.g. that the problem is inadequate temporal resolution of the emissions, or that the inadequacy (whatever it is exactly) covers likewise cellulose. For that reason, the proposed emission factor should be considered, while suggesting cautious application

4.3.2 Fungal Spores

Again, only a handful of measurements are available globally on the atmospheric concentrations of fungal spores. Fungal material consists of chitin, not of cellulose as structural material. Measured concentrations therefore add to the "plant debris" discussed above.

Fungal spore counts in the Vienna area which have in part been taken concurrently with cellulose measurements can be considered as a basis (Bauer et al., 2006a, 2006b). In contrast to cellulose, spore counts display a distinctive seasonal pattern, with a clear minimum in wintertime and a maximum in summer (Fig. 11). PM10 mass (not displayed) shows a seasonal pattern with a maximum in winter, such that spores contribute little during the time of high PM pollution.

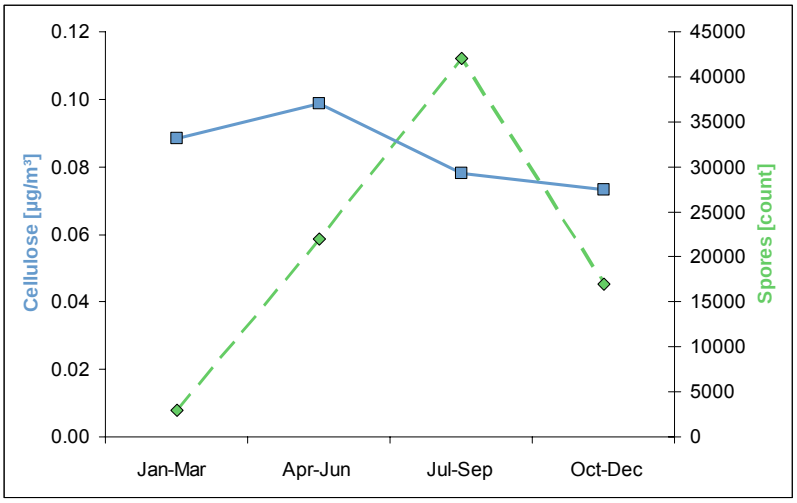


Fig.11: Seasonal cycle of cellulose and spore counts (dashed line) in Vienna

The spore counts have been converted to mass assuming an average C-content of 13 pg C (Bauer et al., 2002), 50% C per dry mass, and a water content of 20% of the spore (Sedlbauer and Krus, 2001), yielding 33 pg mass per spore. Assuming a density of 1, this mass is consistent with the mass of a sphere of 4 µm diameter. The size conforms to microscopic evidence (Wittmaack et al., 2005). At spore counts averaging 25000 per m³, almost 1 µg/m³ of observed PM10 concentrations may be attributed to spores. Depending on the specific circumstances, spores make up between roughly 0.5 and 5 % of PM10. Highest contributions are in summer distant from cities, the lowest contributions in those periods relevant for PM10 thresholds: urban winter situations.

Comparing Plant debris data (from cellulose measurements) and fungal spores, an emission rate can be derived. Fungal spores occur at the same concentrations up to about five times the concentrations of plant debris. The difference may mostly be attributed to the seasonal cycle of fungal spore counts. We use an average factor of 3 resembling the annual mean. Applying the plant debris emission factor of annually 6 kg/km² leads to an estimated 18 kg/km² emissions of fungal spores per year. The same area (total area less barren land and water) seems relevant as for plant debris.

While applying data from just one city to all of Europe seems far from representative, we can only use a few sets of measured concentrations to validate our assessment. Graham et al. (for the Amazon forest) report spore counts resulting in 0.3-3 µg/m³ concentrations (high concentrations during nighttime). Matthias-Maser et al. (2000) and Jaenicke (2005) apply a totally different method – dying particles with a protein-sensitive dye, and subsequent microscopy analysis. They arrive at concentrations of total PBAPs between 0.3 (remote areas) and even 6.5 µg/m³. They find the highest concentrations in suburban Mainz, giving another reason not to exclude built-up area as a potential source area.

4.4 Methods to discriminate between PM originating from natural and anthropogenic VOC emissions

Although spatial data and quantitative models describing BioVOC emissions are available, they give no information regarding their contribution to pollutant levels at a certain time at a certain place in Europe, since the composition of ambient air is influenced not only by the strength of the respective sources but a variety of other factors. Current models describing these processes do not reach the appropriate spatial and time resolution. Thus, an analytical method suitable to discriminate between natural and anthropogenic contributions to secondary organic aerosol is a

precondition for both the quantification of natural contributions to monitored PM levels and model validation.

However, to our knowledge, at the moment no measurement technique exists suitable to discriminate between the organic aerosol formed from natural and anthropogenic precursor gases. This is in part due to the fact that degradation of biogenic volatile hydrocarbons in the atmosphere leads to the same products than degradation of organic compounds of anthropogenic origin; moreover, uncertainties in the biogenic emission inventories are still high, and although many efforts are made in Europe for inventorying anthropogenic VOC, only limited studies are available for biogenic ones. For this reason the currently available models are often unable to reproduce many biogenic pollution phenomena.

Organic Carbon is a complex mixture of hundreds of different compounds whose individual concentrations, composition, distributions, and formation mechanisms as well as their relation to different sources are still poorly understood; for this reason it is very difficult to separate the fraction of secondary organic aerosol into anthropogenic versus natural in origin with a simple analytical technique. Apposite radiocarbon (^{14}C) measurement performed on an ambient air sample, along with OC/EC ratios calculations and biogenic SOA tracer measurements, can provide a means for quantitatively distinguishing the separate contributions to carbon from fossil-fuel (i.e. anthropogenic) and non-fossil-fuel (i.e. biogenic) related sources. The method depends on the fact that ^{14}C is present at a small but measurable, approximately constant, level in living materials, but absent in fossil fuels.

Even in cities the contribution of biogenic carbon to total secondary organic aerosol can be considerably high (about 70%), but biogenic carbon is not necessarily of natural origin. SOA precursors produced by wood burning in power plants and households, traffic emissions due to bio fuels and VOC emissions from agricultural plants are of anthropogenic origin but contribute to the non-fossil-carbon fraction. Thus, ^{14}C analysis is not a suitable method to be routinely applied in air quality monitoring networks in order to distinguish between natural and anthropogenic contributions to particulate matter.

Direct thermal desorption gas chromatography – time of flight mass spectrometry (DTD-GC-TOFMS) is an expensive but effective method to analyse organic C-12 to C-40 compounds in PM2.5 filter samples and to identify emission sources contributing to particulate organic matter. Compounds indicating the contribution lubricating oil emissions, oil combustion, wood burning, brown coal combustion can be quantified. A fifth factor or source group with a maximum relative contribution in summer includes plant wax particles (non-volatile bio-aerosol) but also to compounds emitted from combustion sources. BioVOC emissions belong to this source group,

but the analysis yields no information on the contribution of natural and anthropogenic VOCs to the sampled particulate matter.

Aerosol mass spectrometry is an advanced method by which the volatile and semi-volatile PM1 fraction including nitrate, sulfate, ammonium and organic constituents can be measured with a high time resolution. The analysis yields signatures typical for the impact of wood burning or motorway emissions but does not allow to discriminate between the contribution of VOCs of natural and anthropogenic origin. As mentioned above, degradation of biogenic and anthropogenic gaseous organic molecules in the atmosphere leads to the same products, so that the direct analytical discrimination between their relative contributions to particulate matter may be impossible. Anyway, by determining the proportion of non-fossil-fuel-carbon attributable to wood burning, bio-fuel traffic and agriculture, it may be possible in future to attribute the remaining non-fossil-fuel-carbon to natural BioVOCs.

In conclusion, the subtraction of BioVOC contributions to particulate matter from monitored PM-daily mean values can not be recommended, because (1) up to now their impact at a certain time at a certain place can not be predicted by modeling with the necessary accuracy and (2) the existing analytical methods are not suitable to discriminate between natural and anthropogenic secondary organic aerosol constituents.

4.5 Other methods

Advanced research analyses allow a more precise evaluation of natural components and are implemented by various laboratories in Europe.

Many of these procedures have the disadvantage that they require continuous sampling and analysis of a number of components. This results in very expensive procedures that can not be applied as a routine in EU air quality monitoring networks. However the only available methods for the identification and evaluation of natural contributions different from Saharan dust and sea-salt are advanced measurement techniques.

An overview on methods being used for the identification and quantification of contributions by natural sources are described in the following sections.

4.5.1 Lenschow Approach

Figure 12 shows one of the basic information necessary to apply the Lenschow approach, namely the differentiation of different regions / regions types contributing to

local PM concentrations. Hence, one primary information necessary are representative PM concentrations of the corresponding regions.

Figure 12: Source Apportionment of PM according to regions (adopted from Lenschow et al., 2001)

Only mass concentration information will give information as e.g. presented in Figure 13.

Figure 13: Example for mass concentration based source region identification

The actual Lenschow approach further differentiates the contributions of the different regions not only to PM mass, but also to the PM chemical composition. Including the chemical composition of the different investigated regions allows the calculation of compound specific regional contributions as given in Figure 14 on the left side. This figure e.g. shows that the main proportion of the secondary inorganic acid (nitrate, sulphate) has to be attributed to the regional background. Much lower contributions stem from the urban background or local area, as expected.

Figure 14: Example for source apportionment in accordance to Lenschow for an industrial / traffic influenced site

The Lenschow approach finally combines these area resolved information on compound contributions with the emission inventories for PM and aerosol precursor gases (e.g. SO_2) to calculate the contributions by the various source groups as fixed in the emission inventories.
An exemplary result of such an approach is given on the right side of Figure 3 for an industrial and traffic influenced site (Ludwigshafen, Germany; Kuhlbusch et al., 2003). Natural contributions for this site are calculated to be about 7% (2.3 µg/m³) of the total PM10, including soil dust and sea spray.
This approach can reasonably only be applied for longer periods but not for single days. It needs detailed information from both ambient air quality and spatially resolved emission inventories. Hence, this method is not believed to be a method for a day to day approach for the estimation/quantification of the contribution by natural sources

4.5.2 Linear chemical assessment approach

Another approach to derive information on natural contributions by crustal material and sea spray is the use of its chemical composition. Several prerequisites are necessary for the applications of this approach.
- the investigated site should be representative for a larger region, and not be influenced by local activities such as traffic, shipping, or mining

- the chemical composition of PM has to be measured on daily/regular basis

Applying the chemical composition only for inorganic components leads to the neglect of the organic carbon content of soils which can be significant. This problem may resolved by applying local soil composition data including organic matter. Still the regional variability of the soil composition may lead to larger errors not quantified yet.

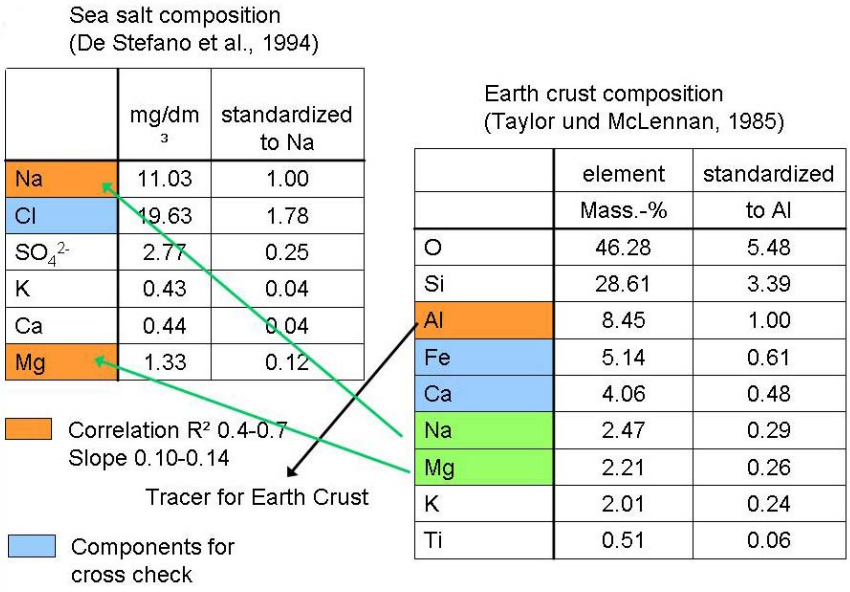


Fig.15 Average chemical composition of sea salt and earth crust material and elements used for the quantification of their contributions to PM

Figure 15 gives the basic information necessary for the calculation of sea spray and earth crust contributions. The major components of sea salt are sodium (Na) and chloride (Cl). Sodium and Magnesium are the elements used in this approach since the latter may be depleted in aerosols due to substitution by nitrate

$$NaCl + NH_4NO_3 \rightarrow NaNO_3 + NH_4Cl \uparrow$$

with Ammonium Chloride being in the gas phase.

The draw back in using Na and Mg for the calculation of sea spray contribution is that these elements are also present in earth crust material. Hence, the contribution of earth crust material is first calculated based on elements such as aluminum, iron, or calcium and the calculated values of sodium and magnesium deducted from the measured values. The remaining concentrations of sodium and magnesium are then used for the calculation of the contribution by sea spray.

		Earth crust	Sea salt	Earth crust	Sea salt	Ca Res.	Fe Res.	Mg Res.	Cl Res.
		µg/m³	µg/m³	% PM10	% PM10	µg/m³	µg/m³	µg/m³	µg/m³
	avg								
rural backg.	Hortenk.	2.05	0.99	19%	10%	0.07	0.04	-0.004	-0.04
urb. backg.	Mainz	2.51	0.93	12%	5%	0.15	0.22	-0.002	-0.04
traffic site	Koblenz	2.94	1.21	12%	6%	0.10	0.53	-0.006	-0.12
traf. + ind.	Ludwig.	4.71	1.00	16%	5%	0.37	0.44	0.004	0.09

≈ 0.5 µg/m³
≈ 0.9 µg/m³
≈ 2.7 µg/m³

March 2002- March 2003

Figure 16: Average PM contribution at the station Hortenkopf (rural background) giving a good fit for earth crust and sea salt material (the values given below the table indicate the local contributions by e.g. traffic and industrial activities)

Figure 16 gives results obtained with this method for 4 different stations (rural background, urban background, traffic, and industrial/traffic hot spot). Only one of the investigated sites is here viewed as being representative for a larger region, the rural background site Hortenkopf. The calculated values fit quite nicely with to the measured leaving only low concentrations of the elements unexplained. It can be seen, that the values for sea spray, stemming from the sea far away are very similar for all sites as expected and indicating the stability of the results. An increase in earth crust contribution can be seen from rural background to the hot spots. This increase is well in the range to be explained by additional emission of crustal material by traffic. The even higher increase for the industrial / traffic site in Ludwigshafen can be explained by the handling of ores in the nearby harbour.

Figure 17: Example of a time series of earth crust material for the sites given in Figure 15

Figure 17 gives and example on the day to day variance of the contribution by earth crust.
The requirements of this method seem to be feasible if specific sites of regional representativeness are chosen and the values of these sites used for the estimate of natural contributions to other measurement sites of the networks.

4.5.3 Wind erosion model approach

The wind erosion approach (DETR, 1999) is based on the assumption that wind blown dust consists mainly of coarse particles. It also assumes that dust only becomes wind blown at wind speeds larger than e.g. 3 m/s and that fine dust concentrations e.g. PM2.5 or finer size fractions are decreasing with higher wind speeds due to higher dilution.
Figure 18 gives an example of the calculation of wind blown dust.

Figure 18: Example for the calculation of the wind blown contribution

The upper graph on the left side shows a fit of the decreasing PM2.5 mass concentrations. The upper graph on the right side is the fit for PM10 mass concentrations. It can be seen, that the mass concentrations of PM2.5 decrease with increasing wind speed while those of PM_{10} at least seem to increase for higher wind speeds.

The difference of the dilution (calculated based on $PM_{2.5}$) and the fit for PM_{10} is the curve shown in figure 18 in the lower left plot. Contributions calculated in this plot e.g. start for a site in Oberhausen (Kuhlbusch et al., 2000) at 2 µg/m³ for a wind speed of 4 m/s

Figure 19 summarizes results obtained for sites in the UK (DETR, 1999) and in Germany (Kuhlbusch et al., 2000). Average windblown dust contributions to PM10 calculated based on this method range around 1 µg/m³ and are about a factor of 2 lower than calculated based on the chemical composition (see section 2.3.2).

Additionally it has to be noted that the method based on wind speed includes all material becoming airborne by wind erosion, hence including organic matter, which is excluded in the estimate given in section 2.3.2.

When comparing the windblown dust contributions for different sites in the UK it could be noted that this calculation is also influence by traffic and other local activities. Hence care should be taken applying this method.

Place	Season	Min. Wind-speed m/s	PM coarse	C Back-ground µg/ Nm^3	C Erosion	Ratio $C_{Eros.}$ / PM_{coarse}	Ratio $C_{Eros.}$ / PM_{10}	PM 10 µg/Nm^3	PM 2.5 µg/Nm^3	$PM_{2.5}$/ PM_{10}	Days of meas.
Lon. Maryl. **Street**	Summer '97	1	14.30	9.55	4.75	33.2%	11.7%	40.73	24.57	69.0%	
	Falls '97	1.5	14.30	12.37	1.93	13.5%	4.9%	39.59	23.34	65.0%	
	Winter '97	2	13.16	9.97	3.19	24.2%	9.2%	34.51	22.80	67.0%	
Hodge Hill '95-'97 **Urban**	Spring	1	9.32	6.58	2.74	29.4%	------	------	------	------	
	Summer	1	9.38	6.78	2.60	27.7%	11.7%	22.30	12.90	53.0%	
	Falls	1.5	8.51	7.57	0.94	11.0%	------	------	------	------	
	Winter	1.5	6.78	5.52	1.26	18.6%	6.0%	20.90	14.50	75.0%	
Average UK 4 sites			**7.41**	**6.15**	**1.26**	**16.6%**	**5.6%**	**20.96**	**14.65**	**68.4%**	
Spellen **Rural**	7-8/'98	2.8	8.09 (1)	6.83	1.26	15.6%	7.5%	21.90	13.36	82.8%	28
	9/'97	4	13.18 (1)	13.02	0.16	2.3%	1.1%	28.97	15.61	47.0%	17
	7-8/'98	3	12.50 (2)	11.22	1.28	13.0%	4.9%	32.18	19.68	62.9%	26
	9/'97	4	12.49 (2)	12.07	0.43	7.4%	3.0%	37.43	24.93	79.9%	36
Ober-hausen **Urban**	2-3/'98	4	11.67 (2)	10.59	1.08	13.4%	3.4%	45.97	34.3	79.2%	23
Duisburg **Urban**, 54 m above ground	10-11/'98	4	8.66 (1)	8.06	0.60	7.4%	3.1%	19.41	10.86	55.4%	24
		3.8	10.95 (2)	10.67	0.28	2.7%	1.1%	30.00	19.05	73.0%	26
Average Ruhr area			**11.90 (2)**	**11.14**	**0.77**	**9.1%**	**3.1%**	**36.40**	**24.29**	**73.8%**	

(1) TEOM measurements

(2) Filter measurements

Figure 19: Wind blown contributions to PM10 given for several sites as absolute values and percents of PM10 (UK sites from DETR 1999)

The requirements of this method, namely the measurements of $PM_{2.5}$ (may be better PM_1), PM_{10}, and wind speed, are feasible. The calculations of wind blown dust contributions seem to be at the lower end of the estimates. Still, this method to sites may not be used for sites with local coarse mode sources.

4.5.4 Multivariate approach, receptor model (PMF)

Another approach for the determination and quantification of natural sources is the use of multivariate receptor models such as UNMIX and PMF (Positive Matrix Factorization). A comparison of various receptor models is given in a paper by Mukerjee et al. (2004).

Data input in the cases for PM source apportionment are normally the chemical composition data for several days, possibly along with some auxiliary information such as rain, wind speed.

PMF uses a weighted least-square fit with the known error estimates of the elements of the data matrix used to derive the weights. The factor model (PMF2) can be written as:

$$X = GF \times E$$

where X is the known $n*m$ matrix of the m measured chemical species in n samples. G is an $n*p$ matrix of source contributions to the samples (time variations). F is a $p*m$ matrix of source compositions (source profiles). Both G and F are factor matrices to be determined. E is defined as a residual matrix, i.e., the difference between the measurement X and the model Y as a function of factors G and F. The factors G and F are derived by best fit correlations of the measured chemical species

Figure 20: Example of PMF results for an urban background site Duisburg, Germany (Quass et al., 2004)

An example of the application of PMF2 on PM10 data is given in figure 20. The data set allowed the differentiation of 8 factors being e.g. related to traffic or secondary inorganic salts.

Receptor models can normally not be applied to not conservative emission. If e.g. secondary components are used in the factor analysis they will not be linked to their sources but will make up a factor on themselves.

The major advantage of PMF is that it can be used for source apportionment studies without prior knowledge on the sources contributing. It compiles the measured data into factors (data reduction) with the factors being separately attributed to sources, either by their chemical composition or by correlation studies with e.g. air mass origins etc. This analysis also gives source contribution data in the time resolution of the data. The advantages e.g. of independent source apportionment is also linked to the draw back that correlation between two source of similar activity can not be differentiated by factor analysis.

One example is given in Figure 20. The factor Sea salt / Holland is mainly determined by its chemical composition (> 80% are sea salt components). Still, a significant mass of this factor is also attributed to elemental carbon and organic matter. PMF could not resolve the two emissions, sea salt and combustion, since whenever sea salt was determined at the site in Duisburg the air masses travelled over the Netherlands. Hence continental emissions such as combustion were always added to the sea salt before it reached Duisburg.

The requirement of receptor models on data availability, data quality, and analysed elements / components are high. It also requires experienced personal to correctly interpret the results of the factor analysis. Hence, even though it is a great tool for source apportionment, receptor model are not seen to be used in the routine work of the measurement networks.

The use of receptor models has recently been extended to organic compounds as well. Some of the components which can be determined with a new analytical device called “DTD-GC-TOFMS” (Direct Thermal Desorption – Gas Chromatography – Time-of-Flight Mass Spectrometry) are listed below:

- PAH – methylated PAH
- Oxidasize PAH
- (n)-alkanes
- Alkane-2-ones
- Long chain Carboxylic acids
- Long chain amides and Nitriles

- Long chain Carboxylic acids methylesters
- Terpenes, steranes, hopanes
- Long chain n-alkyl benzenes and toluenes

This method allows the quantification of organic species / compounds from e.g. PM filter samples which can be related to various anthropogenic and biogenic sources.

These compounds are subsequently used for PMF analysis. First results of a series of filter analysis over more than a year showed reasonable yearly variations of the identified source contributions to PM. Still, further quantitative information on the sources and source strength of the organic tracer compounds are needed.

4.5.5 Single particle analysis, Electron Microscopy

One tool already applied to particles for quite some time is the single particle analysis. Two major tools for single particle analysis can be differentiated, the Aerosol Mass Spectrometer (AMS) and electron microscopy. Figure 21 summarizes some of the tools linked to electron microscopy which are employed in particle characterization studies.

Figure 21: Scheme on the use of microscopy for single particle analysis

This single particle analysis does not primarily derive information based on particle mass but on number concentration. Even though the information may not be as straight forward microscopy is an important tool to assess data misinterpretations such as that of soil dust and fly ash.

Figure 22: Example on the differentiation of soil dust and fly ash only by morphology

Figure 22 shows that the chemical composition of soil dust and fly ash can not be differentiated and that any method solely based on chemical composition data will misinterpret the information either to the one or the other source. Hence it is recommended that electron microscopic analysis should be included in validation studies of source apportionment.

Figure 23: Examples of biogenic primary particles

Figure 23 gives another example on the importance of electron microscopy for source identification, the primary biogenic particles. These particles are accounted for in the chemical analysis as organic matter, or better as organic carbon multiplied by a factor of e.g. 1.4 to account for the hydrogen, oxygen, sulphur etc. being present in organic material. Still the OC fraction is not further differentiated into primary / secondary biogenic carbon or primary / secondary anthropogenic carbon.

Electron microscopy may not be used in the routine network for source apportionment or source apportionment validation, still it is seen as one important tool to avoid or at least estimate the amount of uncertainty in source apportionment studies.

4.5.6 Identification of natural PM by Carbon preference index (CPI) – the example of Saxony, Germany

In a two year joint study between the Umweltbundesamt (UBA) and the IfT (grant number 351 01 031), size-segregated particles were characterized chemically and physically also using five stage BERNER-type impactors.

The size-segregated PM sampling carried out with a sampling velocity of 75 l/min for selected days. The impactors consist of six successive impactor stages with decreasing cut-off diameters (D_{pa}: 10, 3.5, 1.2, 0.42, 0.14, and 0.05 µm). Aluminum foils were used as a substrate (Gnauk et al. 2005). The main aim is to show the differences in particle mass concentration, chemical distribution and physical properties by classification of daily particle characterization results for air masses from west (maritime and/or continentally influenced) and east (continentally influenced) with a distinction between winter and summertime. Measurements curried out at the IfT Research site Melpitz (12°56' E, 51° 32' N, 86 m a.s.l.).

Melpitz is located about 50 km in north-easterly direction from the Halle-Leipzig region (about 1 Million inhabitants) near the city of Torgau, in a representative region for rural sites of the German low lands. There are no major anthropogenic sources of PM near the site (Spindler, et al. 2004). Figure 24 shows the location of Melpitz site and the classification of daily samples for two major long-range transport patterns. The classification of daily samples was based on 96-hour backward trajectories from the NOAA-Hysplit-Modell (source: http://www.arl.noaa.gov/ready/hysplit4.htm). Backward trajectories were plotted twice a day (10:00 and 18:00 CET) and for 200, 500 and 1500 m above ground level for the measurement periods (winters 04/05, 05/06 and summers 05 and 06).

Figure 24: Location of Melpitz site and classification of daily samples for two major long-range transport patterns - air masses from West (maritime and/or continentally influenced) and air masses from East (continentally influenced) and wind rose for the Melpitz site (more than 4.2 million 5 min averages considered, calm wind velocity < 0.5 ms^{-1} in 12 m above ground is 8.6% of the measurement time)

The concentration of n-alkanes is used to distinguish biogenic and anthropogenic sources of carbonaceous PM (Plewka, et al. 2004, Neusüss, et al. 2002). The Carbon preference index (CPI) as a marker for the ratio of natural and anthropogenic emitted n-alkanes, is determined as follows:

$$\frac{\text{mass concentration of odd n-alkanes } (C_{21} - C_{33})}{\text{mass concentration of even n-alkanes } (C_{20} - C_{32})}$$

Alkanes from anthropogenic sources have the CPI close to 1 and the CPI of alkanes from biogenic origins is typically between 5 and 20. Additionally to the CPI index, the mode where alkanes are found can give information on the sources. For example, plant waxes have been found typically in coarse mode PM (Sicre et al., 1990; Kavouras et al., 1998) but fresh traffic emission PM, e.g., is found in the submicron PM. The determination of selected non-polar semivolatile organic species was carried out by CPP-GC-MS (Curiepoint pyrolysis gas chromatography mass spectrometry) directly from the impactor foils. The CPP system (JPS-350, Japan Analytical Industry, Ltd.) acts as a fast thermal desorption injector. The evaporation of species occurs at 500 °C under helium after adding internal standards (two deuterated alkanes).

Figure 25 shows the CPI values as a hint for biogenic hydrocarbons. In summer samples the CPI increases with the size of PM near independently from the source region. The small differences have their origin in the traffic which is the influence from the Leipzig-Halle region. CPI from winter samples (near 1) indicates the anthropogenic origin of the alkanes because the biogenic material was clearly only a minor part of the alkanes and most of hydrocabrons were released from domestic heating and traffic.

Figure 25: Carbon Preference Indices (CPI) from winter and summer and source regions in the West and in the East (every value is a mean of four days)

However the part of natural emitted alkanes in PM_{10} is only a low part and shows a seasonal variability. The analytical procedure for detection is costly and therefore quite difficult for routine measurements.

4.5.7 Summary and comments on described advanced methodology

Various tools for the differentiation and quantification of contributions of natural sources to PM were given. These presented tools and information do not cover contribution from all natural source e.g. excluding vegetation fires and volcano eruptions. An assessment of the feasibility of the methods for use in monitoring networks gives following recommendations:

- The “Linear chemical assessment approach” and the “Wind erosion model approach” seem to be applicable within the networks, if certain precautions are considered and validation steps are conducted. The prior method allows contribution calculation on daily basis, whereas the latter model can only be used for larger data sets.

- The data input requirements for the “Lenschow approach” and the use of multivariate statistics for source apportionment are quite high and hence it does not seem likely that these two methods can be applied on the routine basis. Still, some major advantages should be stressed.
- The “Lenschow approach” gives some general spatial information along with source specific contribution, which is the strength of this approach. Still, this approach can not be used on daily basis and only identifies sources present in the emission inventories.
- The use of multivariate statistics can be used without any prior knowledge on sources and allows for the identification of “unknown” sources. The results are obtained in the time resolution of the data input, hence generally on daily basis in the networks. The two major drawbacks for the general use are the need of educated personal for data interpretation, and the need of detailed and large amounts of high quality data for a good source differentiation.
- Another tool presented was the use of electron microscopy. This tool, even though not giving directly mass based results is necessary to assess data misinterpretation. It also is one of the few tools allowing for the identification and quantification of primary biogenic aerosol contributions.

4.6 MODELING

Model calculations are used to evaluate and to explore environmental policy, and they are essential to the interpretation of measured data. They are an important tool in assessing source contributions to PM_{10}, and even if the current knowledge may not be adequate to account for sea salt and earth crust contributions to PM, they are one of the most important tools in assessing biogenic secondary organic aerosol contributions in Europe. Still, quite some efforts in model validation and extension to other natural sources are necessary.

The use of models, here dispersion models, is recommended to allow for spatial extrapolation of measured values for natural contributions (transport) and especially to enable estimates of secondary organic contributions. The modelled results can normally only be used for e.g. yearly values. Day-to-day variance may not be caught by the models. Hence model results (here dispersion model) may not be used for the consideration of natural contributions on a daily basis. Examples of model applied by some research groups in Europe at regional or global scale are explained in the following paragraphs.

4.6.1 Dispersion modelling

One tool being applied in Germany is the EURAD Model with its structure given in Figure 26.

Figure 26: General scheme of the EURAD Model with the main tool for modelling of the airborne particles (Made) in the centre

The EURAD-Model is a dispersion model mainly consisting of an emission input unit (emissions data plus model), a mesoscale meteorological unit (including orography), and a chemical transport model which includes a submodel for aerosols (MADE). The latter allows to include dynamic aerosol processes such as the formation of secondary inorganic and organic aerosols, but also coagulation and deposition processes.

Figure27: Model results for biogenic secondary organic aerosol for north-western Europe for 2002

The example given in Figure 27 is related to biogenic secondary organic aerosols. This aerosol component can currently not directly be measured but is estimated in campaigns based on e.g. the chain length of alkanes and other tracers for biogenic origin as e.g. analysed by DTD-GC-TOFMS (see section 4). Modelling is especially a powerful tool to derive spatial information on the contribution of ubiquitous natural sources such as biogenic secondary organic carbon (SOA). Biogenic SOA concentrations can be estimated to be between 0.2 µg/m³ and 1.5 µg/m³ estimating the yearly average regional background PM10 concentration to be around 15 µg/m³. Figure 27 shows a similar plot for biogenic SOA but for the year 1995. The concentrations modelled for the same region as in Figure 27 are of comparable magnitude between 0.1 µg/m³ and 1 µg/m³, even though the spatial distribution is slightly different. Figure 28 also shows SOA produced from anthropogenic emitted organic precursors. The concentration derived of SOA of anthropogenic origin are modelled to be generally around 0.1 µg/m³ with a “band” stretching from the channel over Germany to Italy reaching concentrations of around 0.5 µg/m³. Overall it can be noted that SOA of anthropogenic origin is around 10% of that formed from natural precursors if the models are correct.

Monthly average near surface concentration of anthropogenic and biogenic SOA in µg/m^{-3}as simulated with the EURAD/MADE model system for June 1995.

Figure28: Comparison of anthropogenic and biogenic SOA concentrations in Europe (courtesy of Ford Research Center Aachen)

Figure 29 shows results obtained in field measurement campaigns in the framework of the OSOA-Project (Origin and formation of **Secondary** Organic Aerosols). This figure shows the concentration of biogenic SOA calculated based on the SOA-precursor concentrations compared to concentrations of total (biogenic + anthropogenic) SOA.

Fig.29: Fraction of total SOA attributable to terpene ozonolysis

It is evident that the biogenic contributions based on the precursor gases explains only a few percent of the total SOA with concentrations of < 0.1 µg/m³ clearly below those modelled. This difference exemplarily shows the need of better knowledge related to secondary organic aerosol formation and concentrations

4.6.2 Global modeling

Global 3-dimensional atmospheric models can be used to determine natural PM10 concentrations in Europe and allow for the quantification of the import or of these aerosol compounds from other continents. Several methods to determine the natural PM10 contribution from sea salt, dust and biogenic SOA with atmospheric models are described in this study performed by the JRC-Climate Change Unit and the Environmental Chemical Processes Laboratory of the University of Crete.

The proposed methods involve 1.) Modelling concentration fields of natural PM10, 2.) A European aerosol budget, and 3.) Comparison between models using different spatial resolution and parameterisations for the formation of secondary organic aerosols.

4.6.2.1 Introduction to TM4 andTM5

A) Model description

Two global 3-dimensional models are used in this study: TM4-ECPL and TM5. Both are based on the chemistry and transport offline model TM3 [Houweling et al., 1998] having identical physics and using meteorological data calculated by the ECMWF model. In their low resolution mode both TM4 and TM5 have a horizontal resolution of 6°×4° in degrees of latitude × longitude. The main difference is the two-way zooming algorithm used in TM5 [Krol et al., 2004] resolving regions (e.g. Europe, N. America, Africa and Asia) with a finer resolution of 1°×1° degrees. Highest horizontal resolution in TM4 is 3°×2° degrees.

The description of chemistry in TM4-ECPL is significantly different, being more detailed than that of TM5 since VOC chemistry is an updated and improved version of the explicit scheme (molecular lumping) developed by Poisson et al. [2000], whereas the TM5 chemistry is based on the CBM4 chemical mechanism (lumped structure approach). Photochemistry and aerosols are coupled in this version of the TM5 model. The equilibrium model EQSAM [Metzger et al., 2002a, b] is used to calculate the partitioning between the aerosol and gas phases of ammonia, nitric acid, ammonium and nitrate and the water attached to the particle in equilibrium with the water vapour. Sulphate is assumed present only in the aerosol phase. It is formed by the oxidation of SO_2 (and DMS) in the gas phase by OH and in the aqueous phase by H_2O_2 and ozone. Black carbon and organic carbon are externally mixed and assumed to be accumulation particle for the wet and dry deposition processes. Sea salt and dust are externally mixed components in the model; they are described by modal distributions (Aitken, accumulation and coarse mode for sea salt and accumulation and coarse mode for dust).

Both TM4 and TM5 models have a coupled aerosol module to calculate SOA developed by Tsigaridis et al. [2006] that is appropriately linked to the different chemical mechanisms.

B) Emissions

- Emissions of sea salt and dust

Emission estimates for dust are based on simulations with near surface winds of the year 2000 generated by the NASA Goddard Earth Observing System Data Assimilation System (GEOS

DAS). Sea salt daily emission fields are based on the sea salt function following Gong [2003], generated using the year 2000 ECMWF near surface winds. Sea salt and dust fluxes were regridded to a horizontal resolution of 1.0°×1.0° [Dentener et al. 2006a].

- Emissions of nonmethane volatile organic compounds (NMVOC)

The terrestrial biosphere is a major source of biogenic volatile organic compounds (BVOC). For the BVOC emissions, the Global Emission Inventory Activity (GEIA) database [Guenther et al., 1995] for the year 1990 has been used. According to the GEIA database about 503 TgC of isoprene, 127 TgC of monoterpenes, and 260 TgC of Other Reactive Organic Compounds (ORVOC) are emitted annually into the atmosphere. The seasonal pattern of biogenic VOC emissions is accounted for in the GEIA database and monthly averaged emissions are used for the simulations. The rate of isoprene emission is scaled by the daily variation of photolysis rates in order to mimic its dependence on temperature and light [Howeling et al., 1998].

Apart from BVOC, Aromatic components have also the potential to form secondary organic aerosols (SOA) [Odum et al., 1997]. The emissions of aromatic hydrocarbons are adopted from the Emission Database for Global Atmospheric Research (EDGAR) version 2.0 [Olivier et al., 1996] for the year 1990. These emissions add up to about 10-15% of all anthropogenic NMVOC emissions.

C) Formation of secondary organic aerosols

SOA is formed in the gas-phase oxidation of biogenic and anthropogenic hydrocarbons in the atmosphere. The global formation of SOA is estimated to range from 2.5-70 Tg y^{-1} with a central estimate of about 30 Tg y^{-1} (PHOENICS Synthesis and Integration Report, Ed. by M. Kanakidou and F. Dentener). The largest fraction of SOA is from biogenic precursors while the anthropogenic SOA is at least a factor of 10 smaller.

TM5 considers SOA formation from isoprene oxidation based on a fixed aerosol yield suggested by Claeys et al. [2004] field studies whereas in TM4-ECPL this is calculated based on a two-product yield parameterisation as suggested by [Kroll et al., 2006]. This recent parameterisation adopted in TM4 that counts for SOA formed during partitioning of isoprene oxidation products to the aerosol phase is leading to higher SOA from isoprene than the TM5-parameterisation. 32% of the total ORVOC emissions contribute to SOA formation [Griffin et al., 1999]. Emissions of monoterpenes and ORVOC are distributed equally between the model compounds α-pinene and β-pinene.

4.6.2.2 Comparison with measurements

The contribution of sea salt, dust and biogenic SOA to the total PM10 has been calculated for Europe with the TM5 model (Figure 30). Sea salt has a small contribution to the continental PM10; however it can be up to 30% in Ireland, Denmark and coastal regions of Western Europe. Over Crete more than 50% of PM10 are estimated to be from sea salt. PM10 levels for dust are highest in the south of Spain (up to 50%). Biogenic SOA is the main PM compound over Norway, Sweden and Finland during summer.

An important evaluation method for atmospheric models is the comparison of the model results with observations from surface stations. Annual averaged organic aerosol (OA) mass concentrations obtained from TM5 runs are compared to observed organic aerosol from 13 EMEP stations in Europe from a measurement campaign that took place from July 2002 to June 2003 (Figure 31a). This comparison revealed a general underestimation of the observed organic aerosol mass. Especially observed OA mass concentration larger than 3 µg m^{-3} is underestimated by the model while lower values are in better agreement.

In a future study, this comparison will be repeated with a model simulation for the period from July 2002 to June 2003. By comparing monthly averages, additional information can be obtained due to the expected seasonal pattern of biogenic SOA with high production rates in summer and almost no production during winter.

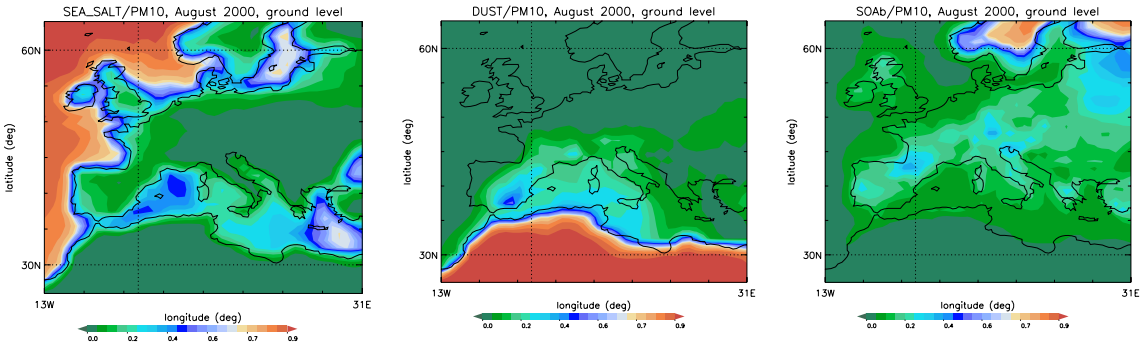


Figure 30: Relative contribution of (a) sea salt, (b) dust, and (c) biogenic SOA (SOAb) to the total PM10 in August 2000 for Europe calculated with the global model TM5.

A comparison for sea salt with measured data from the surface observation network was performed in the frame of AEROCOM (see http://nansen.ipsl.jussieu.fr/cgi-bin/AEROCOM/aerocom/surfobs_annualrs.pl). Over Europe there is a good correlation between modelled and measured values (figure 31b), but TM5 overestimates observed sea salt surface concentrations.

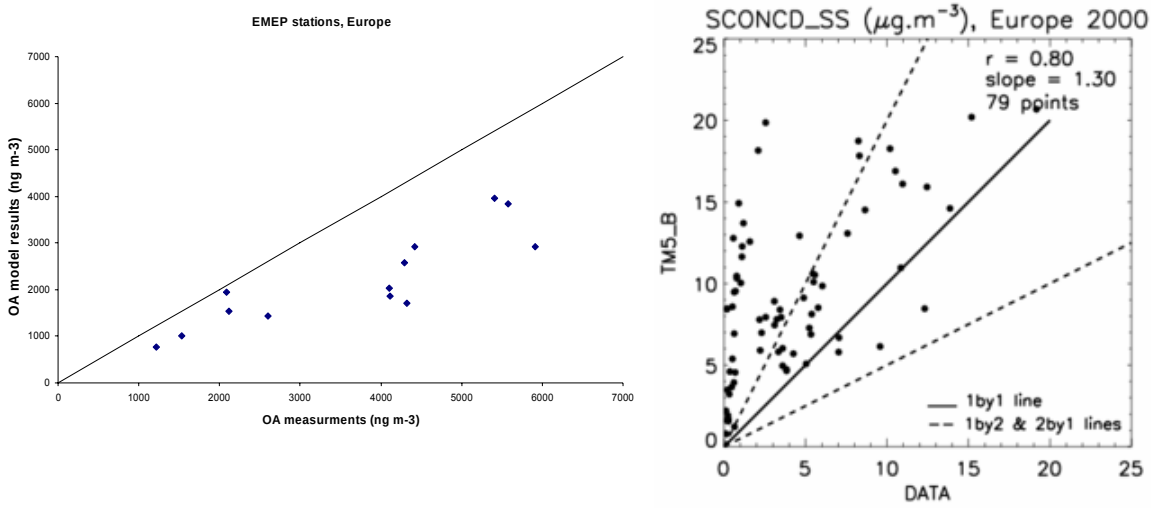


Figure 31: a) Comparison of yearly averaged aerosol phase Organic Aerosol (OA=POC+SOA) from TM5 (1°×1° grid) for the year 2000 with observations from 13 European EMEP stations (July 2002 to June 2003). Solid line denotes the 1:1 ratio.
b) Scatter plot of modelled surface sea salt concentrations (in μg m^{-3}) versus measurements for Europe, yearly average in 2000.

4.6.2.3 The European aerosol budget

The calculated yearly averaged burden of natural aerosols in the atmosphere over Europe is 209 Gg for dust, 71 Gg for sea salt and 8 Gg for biogenic SOA. Concerning the import and export of aerosols from Europe, the net import of sea-salt aerosol (from the west) is calculated to be 10.4 Tg y^{-1} and dust aerosol (mainly from the south) is 37.8 Tg y^{-1}.

Europe is a net producer of biogenic organic aerosols with a production rate of 280 Gg y^{-1} and a net export of 60 Gg y^{-1} (to east, north and south).

Table5: TM5 dust, sea salt and biogenic SOA budget (yearly averages) for the atmosphere over Europe:

Processes	**Dust (Tg y^{-1})**	**Sea Salt (Tg y^{-1})**	**Biogenic SOA (Gg y^{-1})**
Wet+dry deposition	-31.2	-21.6	-230
Sedimentation	-12.7	-60.9	0
Emission / chem. prod.	6.2	71.7	280
Advection, West	1.3	17.0	920
Advection, East	-24.3	-2.4	-810
Advection, South	62.6	-1.7	-120
Advection, North	-3.0	-2.5	-50

Negative sign means loss or export out of the European model region.

4.6.2.4 Sensitivity of modelled secondary organic aerosol concentrations to the model resolution and production parameterisation

Figure 32 reveals the difference for surface concentrations of biogenic SOA over Europe for different model resolutions for TM5. The highest horizontal resolution of 1°×1° degrees tends to give higher maximum concentrations over Italy and Scandinavia.

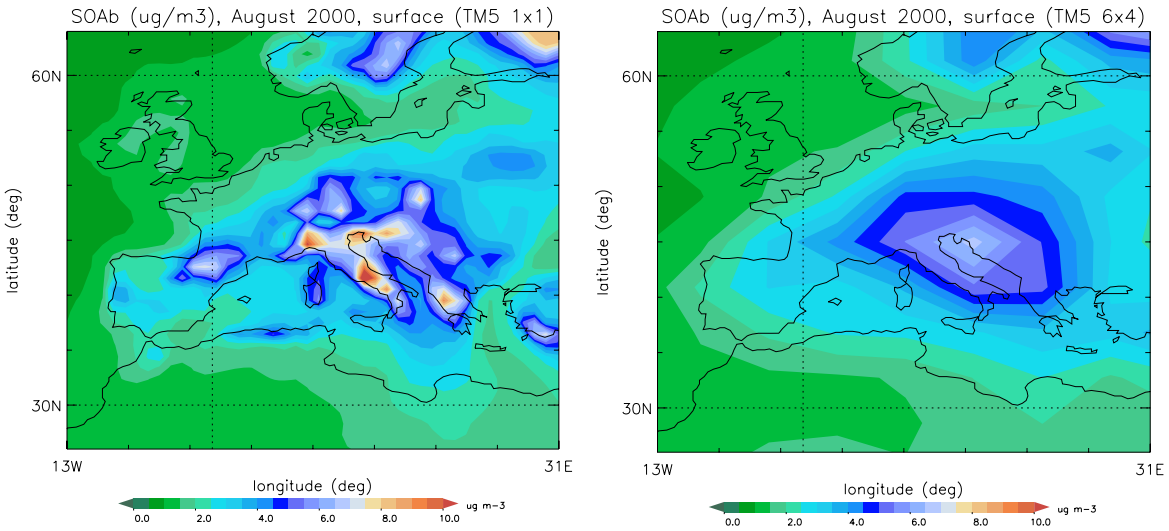


Figure 32: Sensitivity to model resolution in TM5: Biogenic SOA (SOAb) with the horizontal resolution of a) 1°×1° and b) 6°×4° for August 2000.

The result obtained fromTM4-ECPL for biogenic SOA on a 6°×4° grid resolution looks very similar to the TM5 result with the same resolution (Fig. 4b). The maximum surface concentration of total organic aerosol (OA) in TM4-ECPL is located over Poland while it is over South-Eastern Europe in TM5 (Figure 33).

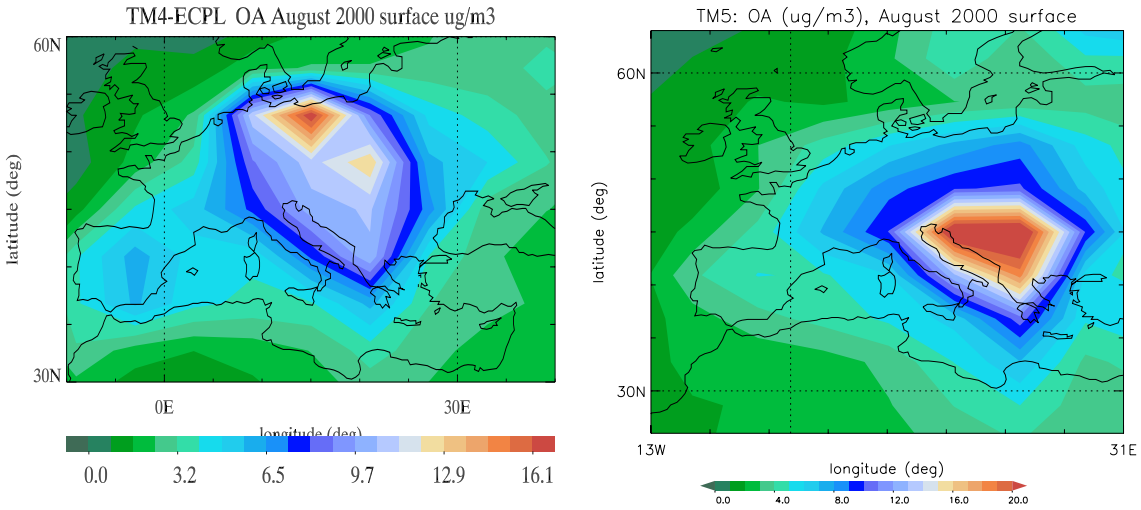


Figure 33: Comparison of organic aerosol surface concentration between a) TM4-ECPL and b) TM5 for August 2000 on a 6°×4° grid resolution.

As an overall remark, TM5 and TM4-ECPL oxidant field simulated distributions differ within the range of uncertainty estimated during recent model intercomparisons (Stevenson et al., 2005; Dentener et al., 2006b). The differences in the oxidant distributions as well as the SOA parameterisations are expected to reflect on the SOA simulations. Synergistic use of the two models is increasing the robustness of the results and the conclusions of the study.

4.6.3 NAME model – UK Meteo Office

In UK the Meteorological Office dispersion model NAME is used to study the origins of the observed high particle concentrations. Assuming a source in Africa, the model is able to explain the timing of the PM_{10} episodes at the different sites across the British Isles with close correspondence. Volcanic eruptions may also be followed using the NAME model.

5. PM emissions from natural events – The NatAir project

5.1 Summary

This work contributes to the identification of a conceptual boundary for the contribution of natural sources to PM levels in Europe from the NATAIR view. NATAIR, a 6th Framework Programme policy support project attempts to assess emissions from natural sources.

First of all it was identified which sources were included, and which sources left or refer rather to national authorities and emission inventories. A first selection of potentially natural emission sources comprises sources that are out of scope of standard national emission inventories. These sources have been investigated to decide if they are dominated by anthropogenic activities, or if they should rather be considered out of human influence. As a means of differentiation, the concept of “human appropriation” was applied. The concept attempts to use surrogate information in order to quantify the human impact. In addition, common schemes of emission reporting guidelines (for greenhouse gases as well as for air pollutants) were investigated, and the reporting practice of emissions from those source groups was also considered. These two issues reflect to some instance the willingness to adopt an emission source as a topic of national interest – a precondition to obtain data as national information.

Among the sources investigated, forest fires and pets clearly seem to be most pronounced to be reported by countries rather than a super-country exercise. These activities and the associated emissions are most strongly influenced by humans. Thus we recommend the emissions to be included in national reporting rather than being considered as natural. Still under considerable human impact are emissions from wild animals and from natural grassland. These sources may also be considered to be dominated by anthropogenic activities, but currently should remain within the scope of this project.

5.2 Introduction and Terms of Reference

Emission inventories describe the material flow of compounds into the atmosphere. Atmospheric transport and transformation processes depend on the amount and the spatial/temporal pattern of emissions, driving the atmospheric concentrations, and on the properties of a respective compound. They do not depend on the type or characteristic of an emission source, apart from its concentration.

Consequently, as seen from an atmospheric perspective, there would be no reason to differentiate between natural (biogenic, geogenic) and anthropogenic emissions. Seen from the assessment of emissions, a number of reasons occur, however:

- Anthropogenic emissions, especially those at high emission density, are often better understood and easier to quantify.
- Background information such as statistics to derive activity data is generally more easily available when human interests are concerned. The reason is that an anthropogenic activity usually is more strongly in human interest than natural activities.

- Activities towards emission abatement can be performed on anthropogenic emissions only. Tampering with material flows from natural source to reduce emissions will affect these sources, and this human activity applied to the source will make the emissions part of the anthropogenic domain.
- With a concept of a polluter and his responsibility for any damage, emissions can be ascribed to a person or a legal entity. Organization or countries thus can be held liable for their emissions, but they may argue that they are not responsible for natural activities. This is also the background why international reporting of “natural sources” is being performed differently to anthropogenic sources, and many countries consider natural emissions to be out of their scope of reporting.

For the reasons given above, natural emission estimates may not be as readily available as estimates on anthropogenic emissions. Thus, increased efforts are required to also assess natural emissions.

In order to assess the overall flux into the atmosphere it is important to acknowledge what actually is included in the current practice of emission reporting, and what is missing. It is one pragmatic option of discrimination to refer to those sources which are not covered in standard inventories as natural sources. Alternatively, one may also try to obtain a better theoretical foundation for such a differentiation and obtain a sound definition of nature, natural processes and natural emissions.

For the purpose of this report, it seems most appropriate to ultimately provide a clear guidance of sources to be considered and others which should be excluded among natural sources. The system boundary to be defined needs to remain practical to be generally acceptable. At the same time it also has to be sufficiently general to allow boundary definition of areas not explicitly defined before. The general acceptability of the suggested methodology needs to be tested against external users.

In the NatAir project, all potential sources for transfer of matter into the atmosphere will be assessed and methods will be developed to quantify the respective anthropogenic impact. This will lead to a comprehensive list of sources ultimately to be considered (the system boundaries between “natural” and “man-made” sources). The approach will consider the fact that a distinct differentiation may not be possible in all cases and a split into the anthropogenic and the natural aspect of a certain emission source will be required.

5.3 Concepts to differentiate the degree of human influence on emissions

5.3.1 Human appropriation

Let us assume a natural state of a system, and investigate the transformations introduced by human activities. Such activities will alter the response of this system in many perspectives. Some of the material flows will be used by humans. Quantifying the amount of such an appropriation may be a way to assess the degree of human influence.

A primary condition for such a quantification is that it is reproducible, i.e., a clear and if possible an externally measurable quantity needs to be selected. Moreover, at best it closely follows the function of the related question, instead of merely serving as a surrogate.

An example for this principle is given as follows. Natural vegetation is characterized by its biomass. Vegetation biomass is also used as food for humans (and also domestic animals) and thus very well representing the function in question. Biomass growth can be quantified as the Net Primary Production (NPP), a quantity that can be derived most clearly in relation to solar radiation.

The concept has been first described by Vitousek et al. (1986), but strongly been adapted since (e.g., Fischer-Kowalski et al.). Basic principles include to also measure the material flow (metabolism) of society, and the colonization (appropriation) of natural cycles. The latter concept has successfully been applied to define human appropriation of NPP as an indicator in quantifying how closely managed land resembles natural land (Haberl et al., 2001). In this application it is convenient that energy flow (related to NPP) is closely related to the anthropogenic use of land management, food (and thus energy) production.

The application to biosphere-atmosphere exchange has been attempted by Winiwarter et al. (JGR 1999), but proved to be more difficult as anthropogenic influence may have very different and non-linear effects on emissions. NPP appropriation as a parameter may merely seen a distant proxy to describe the system behaviour in terms of emissions, and direct conclusions on the extent of human influence on atmospheric emissions are difficult to derive. Still an assessment of human influence will contribute to a wider picture on where a certain emission should be attributed to.

5.3.2 Emission inventory guidelines

Emission reporting is a mandatory element of two protocols protecting the atmosphere, the Convention on Long-Range Transboundary Air Pollution, and the Framework Convention on Climate Change. Specific guidance has been provided to parties of the protocol (countries) how emissions have to be reported. One important differentiation is drawn between emissions which fall within the responsibility of the respective parties, and those which need (if at all) only reported for documentary reasons.

5.3.3 Reporting practice (natural emissions are complementary to reporting practice)

Despite of the guidance given, the practical reality of inventory submission just for sources that under certain circumstances may not be considered under human influence may be different to the guidelines, or different between countries. For the purpose of this project, it is important to note that all potential sources should be covered which are not appropriately reflected in the national inventories. Such a definition may go far beyond what can be attributed as natural emissions, and may occasionally lead to a recommendation to countries to provide more information rather than including it here.
International traffic (sea or air), which is also excluded specifically from national totals, will not be dealt with as these are clearly anthropogenic activities.

5.4 Sources to be discussed in this framework:

5.4.1 Sources included in the Atmospheric Emission Inventory Guidebook

The Atmospheric Emission Inventory Guidebook (AEIGB: EEA, 2004) is probably the most comprehensive reference of potential European emission sources. Within the category “Other sources and sinks”, a number of sources are reported which should be considered within this project. In a previous version of the guidebook this category was termed “Nature”. The change of name reflects the added attention given to anthropogenic aspects of these emission sources. Here we use a slightly agglomerated version of the original SNAP source sectors, which are characterized by a common emission mechanism:

“VEGETATION”: Natural and semi-natural vegetation -
category includes SNAP’s 1101, 1102, 1104, 1111, and 1112
“SOILS”: NO from soils (natural or agricultural) -
category includes SNAP’s 110117, 110216, 110405, 111117, and 111216
“FIRES”: Biomass burning and forest fires -
category includes SNAP’s 1103
“WETLANDS”: Anoxic soil processes (wetlands) -
category includes SNAP’s 1105, (1106)
Wild animals -
category includes SNAP’s 1107
Volcanoes -
category includes SNAP’s 1108
“GAS SEEPS”: Natural seepage of gas storage -
category includes SNAP’s 1109
Lightning -
category includes SNAP’s 1110

5.4.2 Additional sources

The following sources are also considered to be potentially relevant. For a variety of reasons (lack of information; or not attributable to a single country as being sea emissions) they have not been included in the AEIGB.
“Sea salt”: Dried sea spray droplets
“wind blown dust”, especially from barren surfaces and deserts.
“COASTS”: coastal zones, seas and lakes
This category focuses on sulfur compounds only, which is as such not dealt with in SNAP (SNAP 1106 “waters” refers to N2O emissions due to N in ditches canals and similar)
“Primary Biological aerosol particles (PBAP`s)”
“HUMANS”: pets and human exhalation / perspiration (has to some extent been covered in SNAP 1107 previously)

5.4.3 Sources of the AEIGB, but not included here

Some sources that are included in SNAP are not relevant here, as emissions only concern greenhouse gases (CO2, and N2O):

1106 Waters (N2O from Leakage of N into Waters)
1121 Changes in forest and other woody biomass stock
1122 Forest and grassland conversion
1123 Abandonment of Managed Land
1124 CO2 Emissions and removals from soil (except 10.06)
1125 Other

5.4.4 Unknown sources:

While efforts have been taken to cover all potentially important sources of pollutants that are not clearly of anthropogenic origin, there is of course no guarantee that none has been omitted. In general, two pathways exist how new emissions enter the scientific knowledge base. One pathway is by accidental discovery, mostly of a specifically alarming source specimen. This may lead in the beginning to an exaggeration as soon as the effect actually discovered is being generalized, but will become increasingly realistic as soon as more data become available. The other pathway is from a more systematic search, based on discrepancies between existing source/sink terms and the results of inverse modelling based on atmospheric measurements.
An example of how accidental discovery of a source (in this case: geogenic source of methane) and inverse modelling is being reconciled has been given by G. Etiope (2004). The author only fails to recognize that the source had already been covered by the EMEP/CORINAIR Atmospheric Emission Inventory Guidebook (see also Simpson et al., 1999) as well as in the U.S. Environmental protection agency's documents on the Emission Inventory Improvement Program.
There is a considerable limitation to be acknowledged with respect to inverse modelling. Specifically, uncertainty becomes large when deposition and other removal/transformation processes become dominant. Inverse modelling is particularly successful with long-lived gases on the global scale and has been applied towards greenhouse gases. The only greenhouse gas considered here (as it also has its role in photo-oxidant formation) is methane (see above). Similar studies on air pollutants on a smaller scale frequently suffer from the dominance of anthropogenic emissions - uncertainties involved there are often so high that a contribution of potentially missing sources would not be identified.
So the best approach to cover at least as many sources as possible is to watch both the scientific and the technical literature, even if estimates contained therein may be grossly unrealistic.

5.5 Specific assessment:

5.5.1 Human appropriation

I. VEGETATION:

Emissions from vegetation cover primarily volatile organic compounds other than methane (NMVOC) as a side product of the natural metabolism of plants. Still for many plants their metabolism is fully governed by anthropogenic activities. Therefore emissions from “crops” have *a priori* been considered under agriculture. Instead, we will discuss here only vegetated area which is generally left to itself.

Natural grassland: Grassland in Europe is typically used as pasture or even for harvesting. Biomass is fed to domestic animals and thus used for anthropogenic purposes. This is also the case for many remote areas – the AEIGB reports on the biomass cycle of grass cutting on “natural alpine meadows”. Animal grazing and grass cutting prevents the formation of scrubs.

Scrubland: Chaparral and scrubs are widespread plant communities in many parts of Europe, remnants of grassland, possibly after a previous forest clearing. While normally not used by humans, they are a consequence of previous anthropogenic land use patterns.

Forests: Forestry is an important economic sector in all countries that have extensive forests. While trees are left for themselves for most of their lifetime, logging (or at least removal of fallen wood) is performed for economic use of a considerable proportion of biomass. Intensity of cultivation differs. One extreme is energy plantations and Christmas tree production, having a fast turnover of a few years only and also involving forest fertilization. The other extreme is the largest primeval forest in Europe, Bialowieza Forest of Poland.

Comparing data presented by Haberl et al. (2001) for above-ground net-primary production (NPP) in Austria with harvest data shows that in agriculture about 89% of biomass production are harvested, in grasslands 56%, 26% in forests and only 5% in Alpine areas (scrubland). In order to assess human appropriation, a comparison to the NPP of the potential vegetation would be required, which is not explicitly available by source type in the paper. Still the numbers provide a good indication to which degree the respective activities are human-governed. As the potential vegetation NPP is quite different only for agriculture and grassland, only the shares of these anthropogenic activities would strongly increase. On a European scale, the difference would also affect scrubs as the natural vegetation may also include forest, which is not the case for Alpine tundra.

With this information presented, we consider the degree of human appropriation in forests and scrubland “low”, and “medium” in natual grassland (see Table 1).

II. SOILS

Soils are complex systems involving biological activity in the soil – in interaction with roots and plant community’s above-soil – as well as external inputs, from fertilization as well as from atmospheric deposition. Man-made air pollution contributes significantly to soil nitrogen. Even before plowing and destroying the soil stratigraphy, anthropogenic impact is significant. As it is not possible to differentiate impacts on soil and the vegetation above, we suggest to adopt the human impact from vegetation.

III. FIRES

Forest and scrubland fires are a major issue in Mediterranean air quality considerations. In dry summer weather, wood ignites and strong winds fan the fire additionally. Incomplete combustion at the typically very instationary conditions leads to the release of considerable quantities of CO, NMVOC and particulate matter (PM). In addition to air quality problems, fires also jeopardize property.

In contrast to the vegetation emissions from the same area, there is a clear cause for forest fires. EEA estimates that clearly more than 90% of all Mediterranean fires originate from human impacts, with the largest share from arson (Stanners and Bourdeau, 1995). Also 87 % of the fires in the boreal region of Russia are started by people (Mollicone et al., 2006).

It remains to be discussed whether – without the set fires – the additionally available dry firewood might lead to an increase in number or intensity of natural wildfires. For the time being we will consider the human impact “high”.

IV. WILD ANIMALS

Animals roaming forests and grassland are strongly dependent on human activities, even while not in direct custody. Without a natural enemy, the number of deer is almost entirely controlled by hunting, and animal numbers in general are derived from hunting statistics. Deer population in general surpasses the natural carrying capacity of land by a considerable factor. As a consequence, deer has to be fed and dispositions have to be made to carry deer over the winter months, even if this endeavor is not necessarily effective (Putman and Staines, 2004). The ratio of a sustainable number of deer in forest and other natural area and the current situation can be used as an indicator of human impact. Definite figures seem to be unavailable, even if authors

agree that these effects are real. If data exists, still the interpretation remains highly controversial (see Young, 2001, and citations therein on a textbook example in Arizona, U.S.). Until better information becomes available, we remain with the textbook example that indicates a doubling of animal numbers from a natural situation to one of human guidance. We understand this “medium” influence may underestimate reality.

V. VOLCANOES

For most countries, volcanic emissions are insignificant, but for some countries volcanoes are the prime emitters especially of SO2. In Europe, this regards Italy and Iceland. In general, volcanic emissions can not be predicted and even less controlled by human activities. There is an exception concerning geothermal power plants, which may be the cause of additional emissions. These emissions should however be reported under energy production.
Consequently, also volcanic emissions are to be considered purely natural.

VI. LIGHTNING

Lightning is a phenomenon that produces pollutants in the atmosphere rather than transferring compounds. The process of lightning and thunderstorm is caused by atmospheric convection, driven by solar energy. Despite some successful attempts, large scale anthropogenic influence (cloud seeding) is not common practice.
Lightning numbers depend on storm intensity, which will increase on higher atmospheric water concentrations and higher temperatures. Climate change is expected to “very likely” increase the heat index (combined temperature and humidity) over land areas (Houghton et al., 2001). Even if these authors insist that their climate models can not predict small-scale phenomena such as lightning, we assume a weak anthropogenic component (“Low”) in the otherwise purely natural source.

VII. SEA SALT

Sea spray and subsequent formation of airborne particles by evaporation is a function of wind velocity. Neither the sea surface area nor wind speeds have been significantly influenced by man. Shipping as a potentially additional source of sea spray is considered negligible. Thus we imply human appropriation of sea salt formation as 0% (“None”). Climate change impacts due to a change in storm frequency and intensity may be possible, but to our knowledge has never been quantified.

VIII. WIND BLOWN DUST

Wind blown dust is the land equivalent of sea spray. Emissions depend on wind speed and soil conditions, with high emissions from barren dry sandy soils. Soil conditions may be influenced by man, as agricultural practice (fallow period, overgrazing) can lead to such barren ground.
A European land use map (PELCOM: Mücher, 2000) assesses about 160,000 km² of barren land in Europe, most of which is in the Mediterranean area (predominantly in Spain). Even if this is desert-like dry land, we conclude that long-term anthropogenic developments contribute to this state, such that at least a third of the area should be attributed to human impacts ("Low").

IX. COASTS

Certain marine phytoplankton are able to convert sea water sulfur compounds (most pronounced: sulfate) into DMS, dimethyl sulfide. This gas is supersaturated in water with respect to the atmosphere, which will cause a net flux into the atmosphere, where at a later stage it will be converted to sulfate again. Production of DMS and other VOSC (volatile organic sulfur compounds) is pronounced in coastal areas, but it has also been observed in sweet water (Lomans et al., 1997). There are indications that DMS production is influenced by nutrient input and also by global temperature change (Matrai and Penner, 2000). More information is required for firm quantification, at this time we estimate the human appropriation at 10% ("Low").

X. PRIMARY BIOLOGICAL AEROSOL PARTICLES

Pollen and plant debris derives from vegetation, which itself is considerably influenced by human activities. We derive human appropriation as a direct consequence of this preceding intervention, even if this consequence is neither desired nor expected. As biomass density is highest in forests and much of pollen and leaves, which contribute to plant debris, derive from there, we apply the same quantification as for forests ("Low"). This may likely be an underestimation of the impact, if also other human impacts (e.g., grinding of plant material in industrial processes and on roads) may be considered.

XI. HUMANS:

In the domestic area, the human population itself and their pets still need to be considered. Pets are excluded from other source categories like "agriculture", as they do not contribute to an economic activity. Still they are clearly and fully controlled by their respective "masters", both in

terms of their number and their excrements. Pets are to be considered in the human realm by 100%.

The high level of sanitation and the separate consideration of emissions from latrines as “waste” in the AEIGB reduce emissions from humans, despite of their large number and overall biomass, to a relatively small contribution to the overall total. Still emissions from exhalation and perspiration (mostly methane and ammonia) also need to be considered. From a systems theoretical viewpoint, one might argue that a system needs to be internally closed, and can not put any constraints on itself. Following this argumentation, we refrain from putting any restrictions on this perspiratory activities and leave it fully out of the human appropriation – even as it may sound somewhat odd that man cannot at all put control upon himself.

5.5.2 Emission inventory guidelines

Two essential reporting obligations exist for most European countries. Being parties to the UN Framework Convention on Climate Change (UNFCCC) as well as to the Convention on Long Range Transboundary Air Pollution (LRTAP) under the UN Economic Commission for Europe, countries have to report national emissions to both bodies. While UNFCCC’ focus is on greenhouse gases, LRTAP is directed towards air pollutants. Guidelines have been developed independently for both obligations, intended to support national experts in their work. Considerable effort went into harmonizing countries’ requirements of input towards those bodies in the recent years.

In both cases, guidance to countries consists of two parts, one of which refers to the technicalities and submission details such as data formats, the other provides the scientific and technical background for emission calculations. The UNFCCC guidelines regarding the national emissions of greenhouse gases (UNFCCC, 2004) draw on the detailed IPCC guidelines (Houghton et al., 1996) and the subsequent good practice guidance also issued by IPCC, the Intergovernmental Panel on Climate Change, acting as the UNFCCC’s scientific arm. Likewise, emissions of air pollutants submitted by countries to UNECE in the framework of the LRTAP convention are expected to follow the UNECE (2003) guidelines. The scientific and technical background to assess emissions of air pollutants is provided in the AEIGB (EEA, 2004).

These guidelines also determine the concept behind the respective endeavour. As already Winiwarter et al. (1999) have worked out by comparing the respective background documents, it is the scope of greenhouse gas inventories to cover emissions that are anthropogenically effected only. Greenhouse gas inventories consider sources and sinks of gases, and they assume that for natural processes the source term and the sink term are identical (being in

equilibrium). Air pollutant inventories, which do not include a sink term (atmospheric deposition of air pollutants is considered elsewhere, as part of atmospheric transport and transformation models), require the consideration of natural emissions, otherwise they would be incomplete. Thus AEIGB contains a specific section for this emission category, titled “Other sources and sinks” and aims at full coverage of all fluxes into the atmosphere, even if not all sources actually are included.

In an effort to harmonize the respective national obligations, the “New format for reporting” (NFR) for air pollutants (UNECE, 2003) closely follows the reporting scheme for greenhouse gases. As a consequence, there is a lack of clear guidance on reporting natural emissions, if this is possible at all. The reporting format only allows for reporting of sector 5E (“Land use, land use change and forestry – Other”) and X (“11 08 Volcanoes”) outside of the national totals – which is where natural emissions conceptually should go. Potentially (or partly) relevant sectors inside the national total (which would be conceptually wrong reporting) are sectors 4D1 (“Agriculture – direct soil emissions”), 5B (“Land use, land use change and forestry – forest and grassland conversion”), and 7 (“Other”). Therefore it is consistent to report volcanic emissions and emissions from vegetation foliage (under X and 5E, respectively), and still possible to report forest fires, assuming they are involved in a land use conversion process (under 5B). Other emissions which potentially are also reported by countries are actually not represented in this scheme.

In the UNFCCC (2004) guidelines, the lack of natural emissions has been an initial concept. It is therefore no surprise that the sources covered in NATAIR are widely missing. As much as land use change is concerned, emissions from forest fires are included. Other than that, no emissions from natural sources are expected to be covered – specifically, as the UNFCCC inventory in the context of land use strongly focuses on CO2, which is not relevant here.

5.5.3 Reporting practice

Specifically differentiating between guidance and practice of reporting already implies that there is a difference between these two. It is merely a consequence to also expect large variations in reports submitted by individual countries on this issue. In the following, we will attempt to identify common patterns which emerge despite of the diverse interpretation of the guidelines, even if this is complicated by the guidelines’ ambiguity in terms of the emissions of non-greenhouse gases.

National inventory reports are available from the UNFCCC web site (http://ghg.unfccc.int/default.htf). We focus on those emissions that are reported by countries under the following source sectors:

Emissions from Biomass Burning (5A)

Changes in Forest and Other Woody Biomass Stocks (5B)

Forest and Grassland Conversion (5C)

Abandonment of Managed Lands (5D)

Other Land Use, Land-Use Change & Forestry (5E)

Other (7)

As expected, emissions relevant for air pollution (CH4, NOx, NMVOC, CO) are only reported for sectors 5B and 5E, and even then for 7 and 8 (respectively) out of 35 countries only. One country consistently reports emissions for sector 7, but none of the other sectors. Even for countries that do report it is difficult to find out to which degree foliage emissions, and to which degree forest fires are included.

An assessment of national emissions submitted to UNECE has been published by Vestreng et al. (2004). This report is based on the national submissions of 2003, for a base year of 2001. Even as this endeavour strongly focuses on pollutants like NMVOC, only a handful of countries actually report the emissions from vegetation. Even as it is difficult to exactly attribute the emissions, we understand that out of 38 countries, four report foliar NMVOC emissions under sector 5E, three under 5B, one under 7, and one as SNAP sector 11 ("other sources and sinks" in different nomenclature). Also, forest fires seem to be reported under 5B (two countries), 5E (one country), as well as 7 and SNAP11 (one country each). It should be noted that most countries do not report any emissions from the sources considered by NATAIR, and among those that do some consider it inside their national total (sector 5B or 7), and some outside (sector 5E, SNAP11).

One country specifically mentions that their inventory includes human perspiration, and add this to category 7 ("Other").

Volcanic emissions have been reported by the country concerned most strongly. Nevertheless, Vestreng et al. (2004) include volcanic emissions as a separate item in their country tables, similar to an item they refer to as "Natural maritime emissions". In both cases, their values have been taken from "expert estimates" for SO2, with no other compound estimated. These latter emissions presumably refer to the same that are reported as "COASTS" in NATAIR. But they merely provide an alternative source to compare emissions to and are not national information submitted officially.

5.6 Discussion and Conclusion

As a result of the considerations above, we will provide an overview of how the NATAIR source sectors are seen in a more general context. Table 6 compiles and compares these considerations. As a first consequence of the categorization, a sub-split of two of the sources had to be provided, as results were so different. This refers to the source "vegetation", which now consists of Forest, scrubland, and Natural grassland, and the source "humans", where we distinguish between pets and humans themselves.

The practice of reporting clearly indicates how important it is to derive emission information in addition to the national submissions. The emission sources that will be studied in NATAIR are rarely included in national inventories, not even as "memo items" outside of the national total. Almost exclusively those emissions are at all included, which also have an identifiable place in the reporting forms – even if ambiguities allow identical sources to be reported under different headings.

Table 6: Criteria to consider sources as human influenced or natural.

	Classification of human appropriation (see section 0)	*Covered by guidelines**	*Reporting*
"VEGETATION":			
• Forest	Low	AEIGB, NFR	Rarely
• Scrubland	Low	AEIGB, NFR	Rarely
• Natural grassland	Medium	AEIGB, NFR	Rarely
Soils	like vegetation	AEIGB only	
Fires	High	AEIGB, NFR, CRF	Rarely
Wild animals	Medium	AEIGB only	
Volcanoes	None	AEIGB, NFR	Yes
Lightning	Low	AEIGB only	
sea salt	None	--	
wind blown dust	Low	--	
"COASTS"	Low	--	
"PBAPS"	Low	--	
"HUMANS"			
• Pets	High	AEIGB only	
• Humans	None	AEIGB only	One case

*) Sources: AEIGB (EEA, 2004); NFR (UNECE, 2003); CRF (UNFCCC, 2004)

The table also shows that guidance on emission estimation is available for many sources, at least in the AEIGB. It is understandable that countries do not take the effort to assess emissions from additional sources, when not required by the reporting guidelines.

Only one source also fits the descriptions of the reporting guidelines for greenhouse gases and thus the concept of an anthropogenic source. This is forest fires. Interestingly, the source is also one out of two in the category of “high degree of human appropriation”, as defined according to the human influence. The other source in this category is “pets”, which may have been overlooked in the reporting guidelines as not being so relevant in terms of greenhouse gases, and/or (wrongly) considered to be included in agriculture (animal husbandry).

Emissions from forest fires and pets are, according to our assessment, clearly caused and regulated by anthropogenic activities. Data are available on a national scale – countries that do have this kind of activities themselves know best how to assess the underlying quantities, needed to calculate emissions. There is no reason why this could be done any better on an international scale. Clearly these two sources, and probably also those termed as “medium degree of human appropriation” (natural grassland and wild animals) should be part of the national total.

Consequently, these sources should not be treated and calculated as natural sources. Within the framework of NATAIR, we decided to keep within the project these activities which are usually not reported by countries. We expect our work will give countries guidance how to assess emissions from these sources in the future, rather than allowing them to back out of responsibility. As emissions are strongly liked to national data, national activities and abatement concepts, inventory quality is expected to rise significantly as soon as reporting of these sources becomes part of the national obligation.

One interesting aspect is that for a clearly natural source consistently very detailed information is available: volcanic emissions are being reported despite being clearly out of human domain. Information on volcanoes exists due to indirect economic aspects (natural hazard) and as a side effect this information provides also to be advantageous for emission assessment.

6. CONCLUSIONS

An important conclusion of the discussions with experts from the Member States was the attempt to define what can be considered as “natural contribution”, taking into account in the definition that, according to EC Directives, it might be deducted from total PM whenever it is causing exceedences of limit values.

Accordingly, for the purposes of compliance to air quality limit values, natural source contributions to PM are events that may not be influenced, mediated, hindered, or limited by human action. Such a definition considers as a “natural event’’ sources of PM which are outside of human influence, such as anthropogenic long-range transported particles, but it excludes aerosols formed by the interaction of natural with anthropogenic compounds, as well as all natural emissions that can be controlled to some extent by appropriate human-initiated measures.

With respect to the issue of compliance with Air Quality limit values, the most important PM contributions by natural sources may be summarized as follows.

Wind blown mineral dust transported over long distances and sea salt are the most important natural sources affecting PM levels in Europe. They mainly affect air quality in the Mediterranean area countries, as they are close to arid and semi-arid regions in North Africa (e.g., Sahara and Sahel deserts). However, as extensively presented during the workshop, a multitude of natural sources may affect PM levels at lower, but still appreciable extents. Specifically, the natural particulate-matter sources considered during the workshop and their possible contribution to ambient PM levels were:

- The contribution of transported Saharan dust may reach more than 60% of total PM_{10} in Mediterranean countries during a strong dust pollution event. Dust (both of anthropogenic and natural origin) affects Mediterranean areas even in the absence of these extreme events, contributing up to 30% of background PM_{10} level in some regions.
- Sea-salt may contribute to PM_{10} mass concentration not only in the Mediterranean basin, but with more intensity also in some coastal areas of Northern countries. However, sea spray formation occurs during high wind episodes, in particular in Northern EU: hence, these events occur during relatively low ambient PM_{10} concentration. In practice, days of high PM_{10} levels may be only partially affected by significant sea-salt contribution and therefore sea salt influences annual average more than daily average PM_{10}.

- Primary biological aerosol particles (PBAPs) include individual units as pollens or spores, as well as fragmented material as plant debris. Their contribution to PM_{10} mass levels is very limited in winter time, and may become 5% of PM_{10} in periods when vegetation is particularly active.
- Secondary organic aerosol (SOA) formed by oxidation of biogenic volatile organic compounds (VOC) may be very important, in particular during summer time in vegetated areas. It has been estimated (e.g. CARBOSOL project) that it can account for 40-80% of total carbon in rural areas. However, the most important interaction of biogenic VOC is with compounds that may be both anthropogenic and natural (NO_x and O_3), the associated complex chemical pathways still being an area of active research. Consequently, participants agreed that at the moment it is not possible to identify clearly the portion of biogenic SOA that is completely natural and to eliminate its interactions with anthropogenic compounds. Thus, given current knowledge the possibility to subtract its contribution from measured PM_{10} cannot be suggested and a much more clear picture of the process and its implication on AQ should be gained. However, this would probably not cause any problems for Member States since the BioVOC impact is relatively high in regions where exceedences of PM limit values are rare.
- Biomass burning and forest fires are generally of anthropogenic origin, and in many cases may be controlled with appropriate actions. Member States should therefore communicate this contribution in view of the possibility of deduction only if the emissions are transported from regions outside the Member State.
- Biogenic non-sea-salt Sulfur aerosol was recommended to be taken into consideration.
-Volcanic activities are limited to restricted areas in Europe and are infrequently causing exceedences of PM limit values.
- Re-suspended particles are a critical issue, since they may be natural in origin (crustal dust) and re-suspended by human activities, or originally anthropogenic. As these two contributions may hardly be distinguished it was agreed that re-suspension could not be accounted for in total PM deductions.
- PM of other natural sources that originate outside of the EU that are transported over long distances into Europe should also be considered. Androgenic pollution events outside the EU which contribute to elevated air pollution levels in the Member States could also justify such an exceedence for the purposes of compliance with EC law, however, this is a distinct issue outside the remit of this report and which would need to be notified to the Commission on an ad-hoc basis..

A number of methods for apportioning fractions of PM to natural sources are presented in this document and were discussed with experts. Accordingly, the apportionment may be done using different methodologies: 1) using routine methods, 2) using information in parallel from background stations and 3) using advanced tools implemented by research groups.

A feasible method for the evaluation and quantification of natural contribution to PM is routine monitoring through simultaneous measurements of PM_1 and PM_{10} concentrations. This methodology is based on the observation that mineral dust and seas salt, the most important natural source contributions to PM, are mainly in the coarse fraction (>90%). Hence, an increase of the coarse-to-fine PM ratio may be indicative of a natural event. In fact PM_1 measurements, whose major components are of anthropogenic origin, would eliminate the contribution of sea-salt and dust (as well as of re-suspension), which are mainly (>90%) in the coarse fraction.

Once a natural event has been identified (by observing an increase in coarse/fine ratio), the nature of the event may be detected by chemical analysis of metals, ions and carbon compounds, quantifying the PM components that have a natural origin. This type of analysis is fundamental also associated to source apportionment studies and for multivariate receptor models, which are normally used for the identification of pollution sources.

For the identification of a natural event (e.g. dust) or an intrusion of transported pollution (as forest fires or biomass emissions) there are different types of advanced research methods:

A) Experimental analysis:
   - source apportionment studies (e.g. using the Lenschow approach, multivariate PMF etc)
   - chemical assessment approach and Mass closure analysis
   - C^{14} measurements
   - Single particle analysis
   - SEM measurements for the identification of biological particles etc.
   - Aerodynamic Aerosol Mass Spectrometer

B) Satellite imaging (e.g. MODIS), LIDAR observations

C) Modeling tools
   - analysis of backward trajectories (available from NOAA Hysplit model for example)
   - analysis of surface dust maps model generated (as from NAAPS or DREAM models)
   - Wind erosion model approach
   - Chemistry-Transport Models at regional (e.g. EURAD) and global (TM4 andTM5) scales
   - NAME model from UK - MET Office

The A) and C) methods are advanced tools implemented by various laboratories in Europe.

Many of these procedures have the disadvantage that they require continuous sampling and analysis of a number of components. This results in very expensive procedures that can not be applied as a routine in EU air quality monitoring networks. On the other hand, the modeling tools are still too inaccurate to provide data to quantitatively confirm or reject the cause of the exceedences of the limit values.

Only few Member States are implementing procedures at a routine level. These are based on the comparison of the available data from air quality monitoring networks from regional background sites and urban/industrial agglomerations. The above meteorological, satellite imagery and modeling tools are widely used to detect natural PM episodes. Once the days with the influence of the natural PM contribution are identified, these are evaluated to identify days recording exceedences of the daily PM10 limit value in urban agglomerations. For the days meeting the two requirements, levels of natural PM contributions measured at the regional background monitoring sites are subtracted from the levels measured at urban agglomerations in order to determine the natural or anthropogenic origin of exceedences. This procedure is applied by a few state members for African dust outbreaks.

The estimation of natural sources by routine measurements performed in monitoring networks being difficult, it is therefore suggested that Member States, whenever and wherever possible, take advantage of experimental observations of advanced continental background stations (WMO) in order to provide the authorities with quantitative evaluation about the extent of natural sources in the calculation of annual and daily averages of PM.

Workshop participants observed that ambient air quality in some countries does not depend significantly on infrequent peaks of particulate-matter concentrations due to rare natural events, but rather it exhibits a constant high background level of natural PM. In these cases it would be more appropriate to consider the possibility to subtract the natural components from measured PM values from annual average instead from daily values.

More importantly, and as argued extensively during the workshop, PM_1 is the most appropriate indicator of anthropogenic PM emissions. PM_1 measurements would render unnecessary the necessity to subtract the contribution of sea salt and mineral dust from routinely reported values as their contribution to PM_1 concentration is minimal, even if a change in the legal metrics of PM from the actual PM_{10} and $PM_{2.5}$ to a future PM_1 appears not feasible in the near future.

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Title: Contribution of natural sources to air pollution levels in the EU - a technical basis for the development of guidance for the Member States

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ABSTRACT:

Exceedences of air quality limit values represent breaches of Community law which can have significant legal consequences for the Member States. For some existing limit values, such as those in directive 1999/30/EC (1st Daughter Directive), an exceedence which is caused by particular natural sources can be ignored for the purposes of ensuring compliance with Community law.
A new air quality directive proposal is currently being negotiated in the Council and the European Parliament and this is likely to extend this principle to natural (non-anthropogenic) sources of pollution generally so long as the "natural contribution" can be quantified and documented. This could include sea-spray and biogenic organic aerosol amongst other materials. The aim of this report is to document those information and methodologies which are available to permit Member States to determine and document natural sources of air pollution. This information will later be incorporated into specific guidance to be developed by the European Commission in the context of implementing the new legislation once adopted by the Council and the European Parliament.
In this report different types of natural sources contributing to PM levels in Europe are identified according to experts' judgment and based on literature studies. The methods currently implemented by research groups of the Member States for the identification and quantification of natural sources are also described.
The content of this report is based on discussions with experts from various Member States, on the results of a questionnaire which has been circulated to experts of all EU Member States, on available literature studies and on the outcomes of a workshop on "Contribution of natural sources to PM levels in Europe" organized by the JRC in Ispra in October 2006.

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